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XII.—A NEW PHOTO-ELECTRIC AND IONISATION EFFECT.

By U. A. OSCHWALD, *B.A.*, and A. G. TARRANT, *B.Sc., A.R.C.S., F.Inst.P.*

Received October 23, 1923.

(Communicated by S. SKINNER, M.A.).

ABSTRACT.

For the discharge in a neon lamp to start a certain minimum voltage is necessary. This voltage is found to be affected very considerably by light or other ionising agents external to the lamp. This effect is believed not to have been previously recorded.

The writers have investigated the light effect in some detail, and record that it is produced by illumination of any intensity above a very low value (0.01 foot-candles producing an appreciable effect), that it is caused by rays of a broad wave-band in the visible spectrum, with a maximum effect in the orange, and that the seat of the effect is located on the surface of both the metal electrodes, irrespective of polarity.

A similar effect, but one whose mechanism is believed to be different, is found to be caused by rays from uranium oxide and from an X-ray tube. In the latter case it was extremely well marked, so that it is possible to detect by this means X-rays from a very feeble tube at a distance of 90 feet. Certain practical applications of this effect are suggested.

THE experiments described below were the outcome of the accidental discovery of the effect of external illumination on a neon lamp. As the effects themselves may be of some interest, and are in some cases believed to be quite new, they are recorded here with only very brief and tentative suggestions as to their underlying causes and mechanism.

As a preliminary step, the lamp was examined fairly comprehensively from the electrical point of view. This examination forms the subject of another Paper by the same authors, to which reference must be made for accounts of the general electrical properties and behaviour of the lamp, and for the experimental methods necessary to secure consistent results. The same lamp, lamp mounting and current supply arrangements as are there described were used in the experiments described below.

One feature of the lamp requires, however, special emphasis here. As the glow of the lamp is an ionic effect, it may be regarded as analogous to the ionic discharge usually known as the electric arc. In common with the arc, it consists of a discharge between two insulated electrodes, and must be started by some process analogous to "striking the arc." The authors have found that if the voltage exceeds a certain value (about 180 for the lamp used by them) the discharge will start even if the lamp is screened from outside ionising agents, though in this case some delay may occur if the lamp has been idle for a long time.

If the voltage, on the other hand, is less than about 140 volts (for the lamp examined), under no ordinary circumstances will the discharge proceed, nor has it been found possible to start it by means of any external agency.

Between the two limits mentioned, however, it has been found that the discharge will proceed if once started by any external agency. Several of such agencies have

been found to be effective, of which the most remarkable is light. Thus, while the lamp discharge will not start in the dark if the voltage is below 180, it will start if the lamp is exposed to light at any voltage above 164.* It is remarkable that this value is almost independent of the source or intensity of the light if it exceeds a certain minimum, at any rate up to intensities of 1,000 foot-candles.

Under X-rays, on the other hand, the lighting voltage is as low as 143 volts for fairly intense rays. It seems probable, moreover, that the mechanism of the light effect is not the same as that of the X-ray effect.

The presence of radioactive substances also causes the lamp discharge to start below 180 volts, but in this case the experimental data are hardly sufficient to

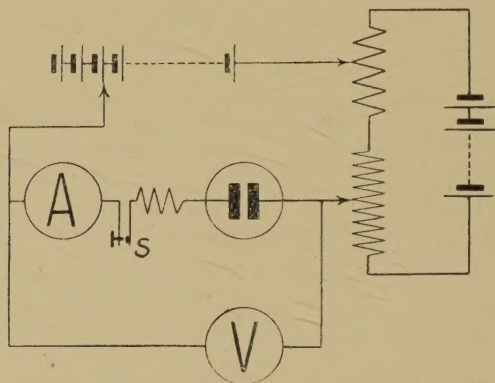


FIG. 1.—GENERAL ARRANGEMENT FOR LIGHT TESTS.

warrant the classification of this effect with the light effect, or with the X-ray effect. The latter is, of course, more probable.

The Paper may be divided into the following sections :—

- I. Observational Methods.
- II. Effect of Light.
 - (a) Effect of varying light intensity.
 - (b) Effect of varying light wave-length.
 - (c) Location of effect inside lamp.
 - (d) Other light investigations.
- III. Effect of X-rays.
 - (a) Distance from tube.
 - (b) Screening by various substances.
- IV. Effect of Radio-active Substances.

I. OBSERVATIONAL METHODS.

The importance of allowing for previous history and for time-change of lamp condition are emphasized by the authors in their report on the electrical properties of the lamp.

* These values, together with all such limiting values quoted in this Paper, must be regarded as subject to a possible variation of one or two volts. In spite of all efforts to standardise lamp condition, the values on different occasions were found to vary by one or two volts, though in any one set of readings they were remarkably consistent.

The following routine was adopted, and found satisfactory in practice. The lamp was switched on for a few seconds, and then allowed to stand idle for a measured period of 120 seconds. The voltage having been adjusted to slightly under the expected lighting voltage, the current was then switched on, and the voltage raised fairly quickly but steadily till the lamp discharge started. The lamp switch was then instantly opened, and the (open circuit) voltage across the lamp noted. The next reading (which might be a repeat of the previous one, or a reading under different external conditions) was taken after a further measured interval of 120 seconds. By this means very concordant results were obtained.

The general arrangement of lamp, voltmeter, switch, batteries, and potential divider, is shown in Fig. 1.

II. LIGHT EFFECTS.

(a) *Light Intensity.*

Preliminary tests showed that very similar effects were produced by all the sources of light tried, which were :

- (1) A 10-ampere carbon arc, with condenser, at a distance of 2 metres.
- (2) A 20-watt tungsten vacuum lamp, at 1 metre.
- (3) A 16-c.p. carbon lamp, at 1 metre.
- (4) A match flame, at 1 metre.

All the above sources of light produced a drop in the starting voltage from 180 to about 162 to 164 volts.

For more exact investigation the lamp was mounted on the photometer-head stand of a photometric bench, and a small 4-volt carbon lamp used as illuminant. For the dimmest illuminations the light was further reduced by the interposition of one or more sheets of ground glass. The illumination was calculated by photometric observations on the source of light (and the obscuring devices, where used) in which it was compared with a 20-watt tungsten lamp.

The effects observed may be tabulated thus :

Illumination							Starting Voltage
(Foot-Candles).							(Volts).
0	182
0 (repeat)	182.5
0.009	180.5
0.018	175.5
0.023	174
0.032	172.5
0.036	171.0
0.072	170.4
0.145	168.5
0.24	167.7
Asymptotic value for brilliant illumination							... 164 to 165 (about)

These results* are exhibited on the curve shown in Fig. 2.

* It must be clearly understood that, consistent as these results appear, it is not impossible that they may be affected to some extent by the rate at which the voltage was raised. Time may be a very important factor, especially at low illumination values—there are theoretical reasons for expecting this to be the case. This point is still under investigation.

(In this connection it may be pointed out that the usual illumination on reading desks, &c., is from 1 to 10 foot-candles. The effect here observed will be seen to be clearly measurable with a light intensity of less than *one-hundredth* of this value. It will also be remembered that measurable photo-electric effects have hitherto required in most cases very intense illumination from arc lamps and very frequently require light not only of very great intensity but very high vibration frequency. The illumination necessary to produce the effect here described is not only very small, but, as will be seen in the next section of this report, need only include rays of comparatively low vibration frequency, i.e., towards the red end of the visible spectrum.)

(b) *Wave-length.*

The above mentioned preliminary tests showed that the effect was apparently independent of the colour of the light used. To study this more closely, the lamp was

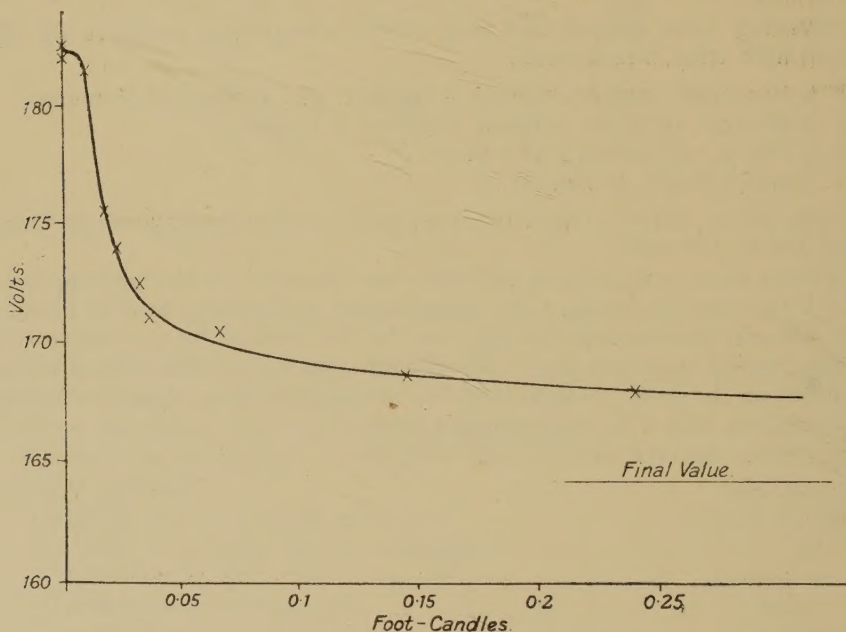


FIG. 2.—CURVE CONNECTING STARTING VOLTAGE AND ILLUMINATION.

enclosed in a wooden box provided with a slit at one end (the camera of a Blondell oscillograph was used). As source of light a 12-ampere carbon arc was used, enclosed in a lantern with a condenser. A slit, lens, and prism were so arranged as to project a large pure spectrum on to the end of the lamp box. The lantern, lenses, prism, &c., were mounted on a table which could be rotated on a pivot vertically under the prism, so that, by turning the table round, any required part of the spectrum could be brought on to the slit in the end of the lamp box, but the angle of incidence on the slit always remained the same.

Inside the lamp box the lamp was so mounted that the narrow beam of light, entering through the slit, fell upon the lamp electrodes, other experiments having shown that this was necessary to produce the effect under observation.

The general arrangement of the apparatus is shown in Fig. 3.

The results obtained were the following :

Part of Spectrum falling on slit.						Lamp. Starting Voltage.
(Dark—arc lamp not running)	{ 178
Dark Red	{ 177.5
Bright Red	171.5
Orange	170
Yellow	166.5
Bright Green	169
Blue	168
Indigo	170
Violet	171
(Full Light, no prism used)	174.5
						162

These results may also be qualitatively expressed in the curve of Fig. 4.

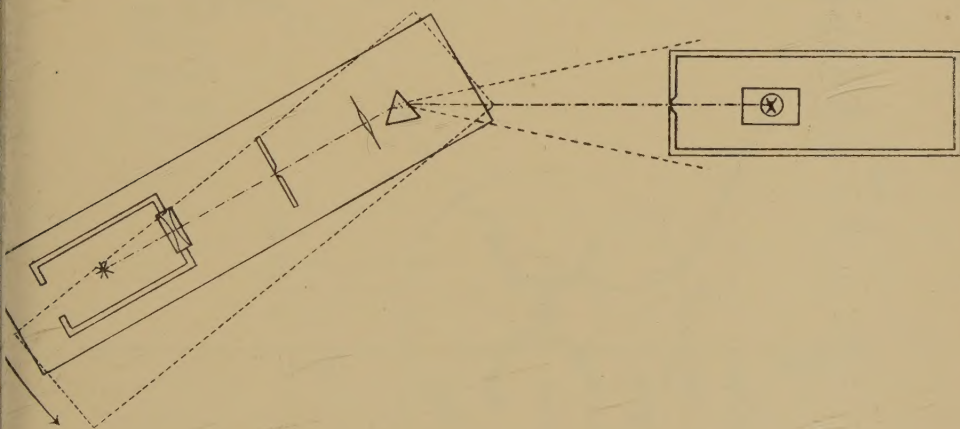


FIG. 3.—ARRANGEMENT OF APPARATUS FOR WAVE-LENGTH TESTS.

Location of Effect Inside Lamp.

With a view to locating the part of the lamp from which the light effect arose, the lamp was mounted as before in an oscillograph camera, fitted with a fine slit at the end, and a second fine intermediate slit near the lamp. Light from an arc lamp was sent through the two slits, and struck whatever part of the lamp was placed in line with them. The outer slit was fitted with an electromagnetic shutter.

The experimental routine for this test was not the same as that above described; the test was carried out before the above mentioned routine had been developed. The results, however, are quite consistent. For this test the time interval between the first instant of exposure to light and the start of the lamp discharge was measured, as preliminary tests had indicated that under feeble illumination there was some delay, which decreased with the light intensity. The standard two minutes rest between observations was given.

In considering the results, the actual arrangement of the lamp electrodes must be remembered. This may be indicated by the horizontal section diagram, Fig. 5. The two outer "wings" form the negative electrode, the inner rod forming the positive.

The various light paths that were used are indicated by the lines A, B, C, D, and E. The results obtained show the following :—

Light Path.	Time before Discharge Started.
A (Missing wings)	Indefinitely large.
B (Striking outer wings) ..	2 to 4 seconds.
C " " " " " " " " " "	" "
D* between centre and side electrodes ...	28 to 40 seconds.
E on centre electrode	2 to 4 "

Each time quoted was determined several times, the observed times lying within the limits quoted.

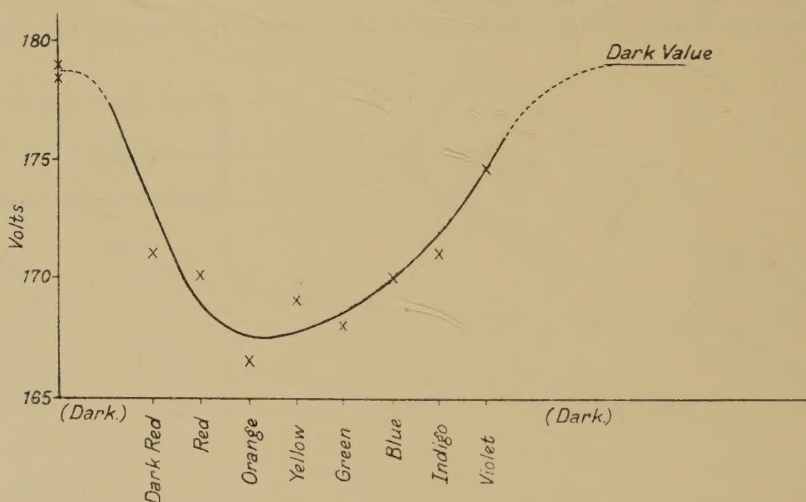


FIG. 4.—CURVE CONNECTING STARTING VOLTAGE AND COLOUR OF LIGHT.

These results show clearly that the seat of the light sensitivity of the lamp must be located on the electrode surface, and not in the gas in the lamp.

It is rather remarkable that no difference was found between the positive and negative electrodes in this respect.

Miscellaneous Light Effects.

"Delay Action" of Light.—It is of some interest to know whether the light effect instantly ceases in the dark when the light is shut off. To study this point, the lamp was placed in the oscillograph box above mentioned, and exposed to light entering through the electromagnetic shutter slit. After long exposure to bright

* It will be remembered that, owing to the very small clearance between centre and side electrodes, it was extremely difficult to prevent the edge of the light beam from touching either centre or side electrodes.

light, the slit was shut and the lamp current instantly switched on. No trace of light effect was detected, showing that the effect ceases very rapidly when the light is shut off.

III. EFFECT OF X-RAYS.

(a) Distance.

To study this effect, the lamp was screened from light by a cardboard box (which would, of course, be quite transparent to X-rays), and exposed to radiation from a small and very soft X-ray tube. The standard experimental routine was carried out.

The following results were obtained :—

Distance between X-Ray Tube and Lamp.	Lamp Starting Voltage.
Infinite (tube not in action)	180
2,700 cm.	174
2,100 cm.	172.5
1,300 cm.	167
1,300 cm.	167.5
800 cm.	165
370 cm.	164 (?)
125 cm.	164.5
31 cm.	164
15 cm.	143

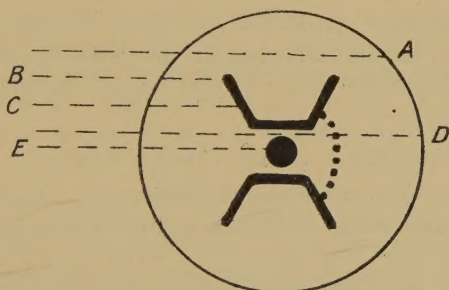


FIG. 5.—PLAN-SECTION OF LAMP.

It will be seen that, with comparatively weak X-rays, it is possible to reduce the starting voltage to 143—a value much lower than the lowest reached by the use of light. (This low value must not be regarded as due to an isolated or “freak” measurement. It was consistently and repeatedly obtained.)

The extreme sensitiveness to very weak X-rays may be noted. Using their very small and weak apparatus, the authors were able to signal over distances up to 90 ft. The possible use of this means of signalling over much longer distances may be here suggested.

The variation of the lighting voltage with X-ray intensity may also be capable of practical application in the provision of warning devices for X-ray workers. A suitable neon lamp, supplied with current from a potential divider and provided with a voltmeter, would provide an extremely simple and convenient means of testing of effectiveness of protective devices in use by X-ray operators.

(b) Screening by Various Substances.

Various bodies were interposed between the X-ray tube and the lamp, which were placed about 25 cm. apart. The results obtained were:—

	Lamp Starting Voltage.
(Tube not working)	184
Tube screened with 2.5 mm. of lead	182
Tube screened with tin plate 0.75 mm. thick	168
Tube screened with aluminium sheet—	
2 mm.	165
4 mm.	166
6 mm.	168
8 mm.	169.5

IV. EFFECT OF RADIO-ACTIVE SUBSTANCES.

The lamp was shielded from light by a cardboard box, and uranium oxide sprinkled on the lamp support. The lighting voltage under these circumstances was found to be 166. After removing the uranium oxide the lighting voltage rose to 183. Thus the effect of uranium oxide is very marked.

No variation of conditions was attempted. But as the radiation from uranium oxide can be regarded as very closely allied to X-rays, it is probable that the same law of variation of effect with distance which applies to the X-ray effect would apply to this case also.

In conclusion, the authors' thanks are due to the Governors and Principal of the Chelsea Polytechnic for facilities afforded for this research, and to their colleagues on the staff of that Institution for certain helpful suggestions made during the course of their experiments.

(ADDENDUM TO THE ABOVE REPORT.)

(Since the above notes were prepared for publication, a further very remarkable fact has been observed, concerning which the writers would beg leave to report in this additional note.)

The lamp with which the above results were observed was in no way specially selected. A "star electrode," British made, Osglim lamp, it was bought with others over the counter from a retailer, and was being shown to students when the light effect was first observed. A Dutch "bee-hive electrode" lamp which happened at the time to be available was also tried, and showed the same effect to a somewhat less marked degree.

As both these lamps were chosen quite at random, and were of different type, manufacture and origin, there seemed no reason to doubt that this effect was a perfectly general property of the Neon lamp. To eliminate variations due differences in details of lamp manufacture, it was decided to carry out quantitative investigations on one lamp only, with results that have been reported above. These results have been observed many times, and the lamp has behaved quite consistently—the light effect, for instance, has been observed upwards of 500 times.

On repeating these tests recently with other lamps of both British and Dutch origin, while all show the X-ray effect to some extent, in no case has the light effect been found to anything like the same degree. In fact, it is not at all recognisable.

in several lamps of recent manufacture. It must, therefore, be regarded as an individual peculiarity of the lamp with which the above tests were carried out.

No reason can be assigned for this except by those to whom the details of lamp manufacture are available, and further study of this effect must be left in their hands. It would be, however, most interesting if any who have lamps available (particularly lamps manufactured during the first few months of British Neon lamp manufacture) would try them for this effect. The writers would be glad to receive news of any in which this effect is at all well marked.

ADDENDUM

(Received May 7, 1924).

It must be clearly understood that the above results were obtained with one and the same lamp throughout. Having no information as to possible changes in the manufacture of these lamps, it seemed well to avoid unknown variables as far as possible by using one lamp throughout. The initial effects were, however, confirmed by repeat observations on a foreign-made lamp of somewhat different type, and the good agreement seemed to indicate that the effects observed were perfectly general to this class of lamp. Some very recent observations, carried out after the above results had been communicated, have shown that some more recently manufactured lamps show no trace of the effect at all, and in some others, while it is apparently present to a much reduced extent, it is shown to such a small extent that it is difficult to be certain of its existence.

These results are in such marked contrast to the exceedingly well-marked and consistent results obtained with the former lamp, and recorded above, that we are forced to the conclusion that some change has taken place in lamp manufacture that eliminates this effect. The matter must be left, therefore, to those to whom details of lamp manufacture are known, for further elucidation.

DISCUSSION.

Mr. J. W. RYDE: I have been very interested to hear Messrs. Oschwald and Tarrant's Paper as I have been working along similar lines myself at various times during the past two or three years. The action of radioactive substances and X-rays in reducing the starting potential of gas discharges is well known. Hemptinne, in *Comptes Rendus*, 1901, showed that the discharge in vacuum tubes began at lower potentials when under the influence of radium. Elster and Geitel in 1899 showed the same for the spark discharge in air. I have not seen the recent German Paper referred to by Mr. Tarrant, but in 1896 Warburg found that in a vacuum tube filled with hydrogen at 11 mm. pressure, with platinum electrodes 4.5 cm. apart, the starting potential was 960 volts in daylight, 1,080 in the light of an arc lamp, 1,260 in the light of an arc *through glass* and still greater in the dark. The effect on the lag was considerably greater, thus when in the dark the discharge did not always pass even when the potential was about nine times that required to start it every time when illuminated from the arc. He does not, however, explicitly state that visible light only would produce the effect.

The present authors mention that they have found that the maximum effect is produced by orange light. I do not see how they can make quite so definite a statement as this as they do not appear to have taken into account the energy distribution of the source they used, especially as in Fig. 2 the magnitude of the effect is shown to depend upon the intensity of the illumination. In the case of radiation from a black body at about 3,000°K. the energy of the yellow is of the order of 10 times that of the violet radiation, so that it is possible that the violet and ultra-violet radiations may be really more effective than the orange.

I first noticed this effect in Osglim lamps in 1921. Later it was particularly obvious when we started to make photographic dark-room lamps by staining the bulb of Osglim lamps a deep

red. Since then, though I have not had the time to study it in much detail, I nevertheless have made a number of observations on it in various forms of discharge tubes.

As I have been able to extend the observations somewhat further than the present authors, perhaps I may be excused if I describe very briefly the principal results.

Warburg and others have shown the considerable effects, produced by impurities, on the cathode fall and starting potential, and it may be stated that in general no reliable fundamental results can be obtained from observations on discharge tubes unless the greatest precautions are taken to purify the gases used.

In consequence, my first investigation was made on the effect in very pure gases, great care being taken to gas free the glass and electrodes thoroughly by baking in vacuo, nearly to the melting point, then running the discharge several times and subsequently pumping out the gas and refilling.

The results were as follows: *Pure helium* with electrodes of Ni showed an average difference between dark and dim light of 1 volt and between dark and very bright light 1 volt.

Pure Ne, He mixture in tubes with electrodes of Fe, Ni, Mn, Al, very doubtful effect, if any. Oxidised iron electrodes were also tried, for reasons which I will mention later, but with still practically no effect.

Very pure nitrogen with Ni electrodes gave very small effect, if any. *Pure hydrogen* with Fe and Ni electrodes was then tried, as, according to Warburg's results, this should show the effect. The starting voltage in the dark was found to be 242 volts, but with very dim illumination it was 9 volts less, and in very strong light 10 volts below that in the dark. Next, mixtures of rare gases were tried with various metals as electrodes, but with no appreciable effect. Thus with a mixture of He and A the starting voltage was 260 volts, both in the light and dark, but in a similar tube having in addition a trace of hydrogen gave 212 volts in the dark and 210 in the light.

Thus the effect seemed to be connected with the presence of hydrogen, so that the next experiments were conducted on mixtures of the rare gases and hydrogen with the following results:—

Argon and 15 per cent. H_2 with Fe electrodes gave an average difference between light and dark values of 5 volts, and with Ni electrodes 10 volts. Ne, He, and 2 per cent. H_2 —

Fe, very brightly polished, showed 3 volts difference.

Fe, surface of electrodes cleaned *in situ* by cathodic sputtering, showed 0 volts difference.

Fe, Osglim star lamp, showed 15 volts difference.

Ni showed 5 volts difference.

When during the manufacture of Osglim lamps a heavy discharge is passed through them to get the gas out of the metal parts, occasionally films are seen to appear on the electrodes. They are of three types, one due to the presence of oxygen, due to a small leak in the apparatus, another is black, and is due to the sputtered metal from one electrode being deposited on the other, and a third is of a pale brown colour, often difficult to see. The cause of the last is somewhat obscure, but seems to be connected with the presence of water vapour and hydrogen.

On trying tubes having these films it was found that those with oxide films gave very irregular results, but those with the brown films generally showed larger differences between the starting potential in the dark and light than any other I investigated. A tube with Ne He + 2% H_2 with Fe electrodes (having brown film) gave a starting voltage of 215 in the dark and 43 volts less in strong light; another gave 182 volts in the dark and 13 volts less in the light. Summarising these results, which are only provisional, we see that the effect of light seems to be connected with the presence of hydrogen in the gas and of certain films (which may be practically invisible) on the electrodes. Further, with very pure gases the effect, if any, is doubtful. Whether the effect is due directly to the presence of H_2 or to the surface films associated with it and water vapour, it is too early to say. The evidence at present, however, points to the latter conclusion. The fact that the authors found the effect in lamps bought some time ago, but not in those of relatively recent manufacture, may be ascribed to the fact that the manufacturers now know more about the effects of impurities and greater care is taken to eliminate them.

Dr. F. L. HOPWOOD said that he had repeated the authors' experiments, as regards the effect of X-rays, with a powerful Coolidge tube. As a result of his experiences he strongly suspected that the lowering of the starting voltage was due to the electrostatic effect of the oscillating potential in the induction coil used in the X-ray apparatus. On screening the lamp electrostatically he found a difference of only a volt or two between the starting voltages with

and without X-rays, whereas he was able to produce a substantial lowering by vibrating an electrified rod in the neighbourhood of the lamp. Using 50 mg. of radium bromide he was unable to reproduce the authors' results as regards the effect of radio-active bodies. He suggested that by using the induction coil without the X-ray tube they might get results similar to those obtained with the tube connected.

Dr. J. S. G. THOMAS congratulated the authors on their striking demonstration. The phenomenon had recently been described* by German investigators, who employed the intermittence effect discovered by Pearson and Anson, which, however, they attributed to a German worker. They found that the period of the flash was affected by light, X-rays and moving electric charges, the frequency varying as the intensity of the light. The phenomenon might furnish a delicate photometric method. It is enhanced by the presence of potassium vapour in the bulb, a fact which favours the suggestion that it is connected with the ordinary photoelectric effect.

The PRESIDENT pointed out that as the authors' Paper had been received by the Society on October 23rd, 1923, and therefore before the date of the German Paper mentioned by Dr. Thomas. He suggested that the point raised by Dr. Hopwood should be put to the test by trying the effect of the induction coil with and without the X-ray tube.

Dr. F. L. HOPWOOD (subsequently communicated): I have now had an opportunity of seeing Messrs. Tarrant and Oschwald repeat their experiments in their laboratory and to carry out similar experiments in my own laboratory. I find the effects described by them are not to be attributed to electrical oscillations, but are true photo-electric effects of the kind fully described and explained by J. J. Thomson in his "Conduction of Electricity through Gases," when discussing Warburg's experiments. My failure to detect any effect other than that due to electrical oscillations was probably due to the fact that the room in which I first attempted to repeat their experiments was contaminated by radio-active deposits formed by the escape of radium emanation, which was known to have occurred some time previously. In another "clean" room, the effects were easily obtained.

AUTHORS' reply (communicated): In the course of his most interesting remarks Mr. Ryde devoted much time to combating the use of the word "new" in our title. We were aware that the effect of light on the high-tension electric discharge had been studied from the time of Hertz and Hallwachs down to the present day. But the results previously recorded differ very widely from those here recorded in scope, nature and degree.

We note with great interest that the lamp manufacturers have already noted this effect. It has been apparently regarded by them, however, as an inconvenient anomaly to be avoided if possible, but scarcely to be published. We, on the other hand, have laid our results freely before this society, and still believe ourselves to be the first observers to bring the phenomenon before the scientific world.

It is rather difficult to see what Mr. Ryde wishes us to infer from his remarks about the energy distribution in the arc spectrum. Does he imply that the effect is due to the *total radiation* from the arc? If that were the case, there would be a maximum in the red or infra-red of the spectrum. If the effect depended essentially upon energy absorption, the energy per light quantum would, of course, be the important consideration, and this would increase almost without limit as we go further into the violet and ultra-violet region of the spectrum. The whole facts of the case seem to point to a selective photoelectric effect as the underlying cause, and the spectrum-effectiveness curve seems to bear this out completely.

In reply to Dr. Hopwood, we fully agree that different lamps show different sensibilities towards light, and, presumably, towards X-rays also. We took precautions that seemed to us to be adequate to guard against electric oscillations, and are firmly of opinion that, while the extreme lowering of the lamp starting voltage when the X-ray tube was very near may possibly be due to electrostatic effects, the lowering produced by a distant X-ray tube is certainly due to X-rays themselves.

We are very sorry that the experiment of removing the X-ray tube, that we carried out before the Society at the suggestion of the Chairman, gave no conclusive results. All workers with the Neon lamp emphasise the importance of using very steady electric supply from batteries rather than dynamo supply, and the supply at this meeting is dynamo-produced and very variable in voltage, irregularities of as much as five volts occurring within a few seconds, in addition

* "Versuche mit der Glimmlampe als Zahlkammer," by O. v. Baeyer and W. Kutzner, Zeit. Physik., 1924, Vol. 21, p. 46. Published January 24, sent in December 9, 1923.

to a most pronounced "ripple." We have invited Dr. Hopwood to repeat these tests in our laboratory at Chelsea.

(LATER.)—On March 26, the above-mentioned experiment was carried out in the presence of Dr. Hopwood and Major Phillips, and a further test performed, whose results are of such interest that leave is asked to include mention of it in this reply.

There seemed little doubt that the effect was genuinely due to X-rays, for it was obtained with the lamp in a fairly complete electrostatic shield. To make matters absolutely certain, a test with radium was suggested, and a supply of radium being very kindly lent by Major Phillips, this test was carried out with the following results :—

One milligram of Radium Bromide was placed near the Neon lamp, which was protected from light by a cardboard box. The starting voltage was found to be about 160. When the Radium Bromide was removed to a distance of about 6 ft., the starting voltage was about 162, and when it was removed to a distance of about 27 ft., and placed behind a piece of lead 2 mm. thick, the starting voltage was 165.

The Radium Bromide being removed to another room, so that it was about 50 ft. from the lamp, with two thick brick walls between the radium tube and the lamp, the starting voltage rose to its normal value of about 180. The following set of tests were therefore carried out in the following order :—

Position of tube containing 1 mg. Radium Bromide.										Lamp starting voltage.
Very distant	181·5
27 ft. from lamp, 2 mm. lead between	165·5
Very distant	182·0
27 ft. from lamp, 2 mm. lead between	165·0
Very distant	181·0
27 ft. from lamp, 2 mm. lead between	167·5
Very distant	182·0

The Neon lamp is therefore an extremely sensitive detector of the presence of radioactive substances, and in the light of these results there seems no reason to doubt that the effect of a very small X-ray tube 90 ft. from the lamp is genuinely due to X-rays.

We must express our most sincere thanks to Dr. Hopwood and Major Phillips for their kind co-operation in these tests, and have great pleasure in putting the lamp concerned at their disposal for the further development, with the greater experimental facilities available to them, of this interesting and possibly useful effect.

XIII.—ON CERTAIN PROPERTIES OF THE "OSGLIM" NEON-FILLED LAMP.

By J. H. SHAXBY, Director of the Viriamu Jones Physical Laboratory, University College, Cardiff, and J. C. EVANS, Eyton-Williams Postgraduate Student of the University of Wales.

Received August 29, 1923.

ABSTRACT.

The characteristic (voltage and current) curve of the "Osglim" neon-filled lamp illustrates many of the properties of the discharge of electricity through rarefied gases. The identity of the sparking potential with that necessary to produce a minimal current through the gas, pointed out by Townsend, is clearly confirmed. Part of the characteristic is negative, and this results in the lamp discharge becoming intermittent on a direct current supply, over a certain range of external resistance, independently of any external condenser in the circuit.

This tendency to a negative characteristic appears, whatever the current through the lamp, when any change is made in the circuit, and this produces instability at the moment of switching on the lamp, and in the case of A.C. supply causes an intermittent discharge during that part of the cycle, when, so far as the supplied volt are concerned, one would expect a continuous glow.

Illustrations are given of the use of the lamp as an indicator in a commutator method of measuring the frequency of alternating currents.

I. INTRODUCTORY.

THE Osglim lamp, consisting of pure iron electrodes two or three millimetres apart in an atmosphere of neon (with small quantities of helium, hydrogen, mercury vapour and other gases), is essentially a low-vacuum gaseous discharge tube; the study of the lamp which forms the greater part of the subject matter of this Paper shows that the peculiarities of its voltage-current characteristic are explicable by the known facts as to electric discharge in gases at the pressure, about 10 mm. of mercury, to which these lamps are exhausted.*

The characteristic curves of the lamps have been described for a range of about 150 to 200 volts by Pearson and Anson,† and by Macgregor-Morris, Doughty and Privett.‡ Pearson and Anson show that for a considerable range the characteristic curve is straight. We have redetermined these curves with great care, and have extended the range down to the smallest currents which will maintain a discharge through the lamp.

II. DETERMINATION OF THE VOLT-AMPERE CHARACTERISTIC.

The readings were made by connecting the lamp in series with a battery of secondary cells, a shunted suspended-coil galvanometer calibrated as an ammeter and an adjustable resistance, by varying which the current through the lamp was

* Ryde, *Photographic Jour.*, June (1925). See also on Neon-Filled Lamps, Moore, *Gen. Elec. Rev.*, 23, July (1920).

† *Proc. Phys. Soc.*, 34, p. 204 (1922).

‡ *Electrician*, Dec. 1 (1922).

controlled. The P.D. across the lamp terminals was measured by an Ayrton-Mather Electrostatic voltmeter.

Simultaneous values of current and P.D. were recorded, in most cases decreasing the current step by step; the few observations made with increasing current were in perfect agreement with the others. There was no evidence of hysteresis, so far as these final steady values are concerned.

A number of Osglim lamps were examined, some containing the ballast resistance which is inserted in the base of the lamp and others without it. In the former case the voltage drop through the resistance has been deducted, so that all figures quoted give voltages between the electrodes. As noted by previous workers the current and voltage for any given source of E.M.F. and external resistance, only settle gradually though fairly rapidly to their final values. When the current is first switched on its initial value is much greater than that to which it finally settles; it may take as much as fifteen or twenty minutes to take up this steady value, and the decrease is most marked at the highest voltages. This is a particularly well marked and protracted instance of the following general phenomenon; on any change of the external resistance the current in its resulting change "overshoots the mark," and then creeps back to a final steady value. The voltage change, on the other hand, does not at once proceed to its full extent, but increases or decreases gradually to its final value. During the settling-down process, in other words, the voltage and current are varying in opposite senses.

Of the two alternatives to take readings immediately after changing the external resistance, or to wait for the ultimate steady state, we chose the latter, because the data thus obtained are definite and reproducible. Those taken just after a change depend a good deal on the magnitude of the change and on the immediate past history of the lamp, as described later.*

Most of the work was carried out with lamps in which the larger electrode is a letter I—i.e., a straight strip of iron, so that the discharge took place between two approximately parallel electrodes. Other forms were also tested, such as the letter W or the Star type, and were found to possess quite similar properties to those of the I type, but the form of the larger electrode introduces some complexities, especially with small currents when the area covered by the glow is shrinking.

Measurements of voltage and current were also made by a potentiometer arrangement. It is to be noticed that the two methods are essentially different; in the first it is the current through the lamp which is directly varied, the P.D. across the electrodes changing accordingly; in the second the voltage is directly controlled, and the current changes as a consequence. The results were in agreement with those of the first method, but it is obvious that the potentiometer method cannot give the portion of the characteristic to the left of the point corresponding to the minimum voltage (Fig. 3.).

III. SPARKING POTENTIAL.

The sparking potential, that is the minimum voltage necessary to start a discharge, was measured at the beginning and end of a test. It is quite definite for a given lamp, though it varies by several volts from lamp to lamp,† and is measured directly by increasing the voltage across the lamp until discharge occurs. This

* See also P. & A., l.c., and M.D. & P., l.c.

† Pearson and Anson, l.c.

may be done either by a set of accumulators the number of which is increased one by one until a glow appears or by using a source of E.M.F. greater than the sparking potential with a potentiometer arrangement. The two methods give identical results.

This potential has also been measured by making use of Pearson and Anson's method of producing flashes.* The apparatus is represented in Fig. 1. If R_1 and R_2 have such values that the lamp is glowing when R is zero, then by increasing R sufficiently flashes will be obtained. Maintaining this value of R one finds the minimum value of R_2 (for any given value of R_1) necessary to start or keep the lamp flashing. The voltage across R_2 under these conditions is the sparking potential. The experiment can be carried out with any value of the capacity or of the resistance R , provided the latter is large enough to give flashes. The values thus obtained proved to be independent of both R and C , except when C was zero, and to be iden-

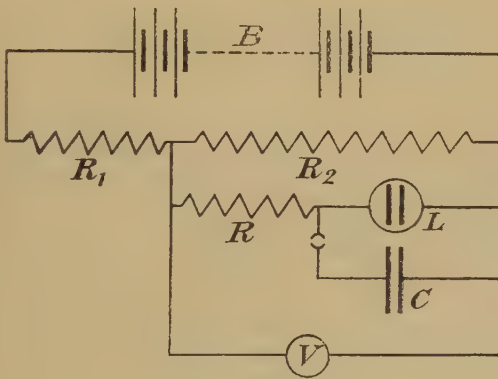


FIG. 1.

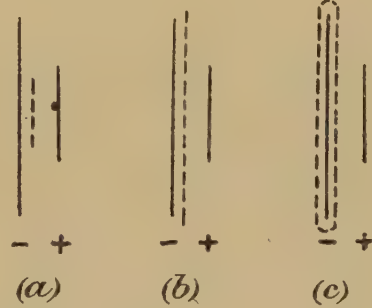


FIG. 2.

tical with those obtained by the previous methods. In the case when C is zero, so that only the capacity of the lamp itself is present, the lamp can be kept flashing with a lower value of R_2 than in the other cases.

The value of R necessary to obtain flashes depends on the capacity in parallel with the lamp. For a particular lamp this dependence is shown in the annexed table.

C	Zero.	Voltmeter.	0.0002mfd.	0.1mfd.	0.5mfd.	1.0mfd.
R	510,000	490,000	460,000	307,000	301,000	300,000

In the first three cases the value of R is very definite; diminution of R by as little as 1,000 ohms (i.e., by less than 0.2 per cent.), changes an intermittent glow to a continuous one. In the last three cases, however, the value is not nearly so sharply marked, but depends on how the limit is approached. The values given are those obtained when the lamp is allowed to settle down by running for a short time after each of a series of small increases of R . In each of these last cases, when the intermittence has been established, R can be decreased to about 250,000 ohms before the glow becomes continuous again.

* Pearson and Anson, l.c.

IV. MINIMUM POTENTIAL.

The minimum potential difference which will maintain a current through the lamp is best found from the characteristic curve—i.e., from the data gained in the first method described above; this gives the rock-bottom minimum. It may, of course, also be measured by the potentiometer method. The first experiments of this latter kind showed variations of as much as 5 volts, the particular figure obtained depending on the immediate past history of the lamp. A very slow decrease of voltage gives the lowest value—e.g., 133 volts in the case of the lamp of Fig. 3. By the potentiometer method this lamp gave an average value of 136 volts; a sudden drop of voltage from 155 to 138 often, but not always, extinguished the glow. These experiments with sudden drop of voltage were made by closing a plug-key which short-circuited some of the cells of the battery. The effect on the limiting voltage of the magnitude of the sudden drop is shown in the table, in which V_1 is the initial voltage and V_2 that final one which just failed to cause extinction.

V_1	150	137·5	133
V_2	140	136	133

When the drop in voltage occurs the area on the electrodes covered by the glow contracts immediately to a very small area, if the drop is not quite sufficient to extinguish the lamp; it then expands again, rapidly in the case of the higher voltages, slowly in that of the lower, the final appearance being the same as would be obtained by a very gradual decrease to the final voltage. Fig. 2 illustrates this in the case of the pair of voltages given first in the table; the continuous lines represent the electrodes, the broken ones the glow. (a) Shows the contracted glow immediately after the voltage is decreased; the stage (b) is then gradually reached, with the glow extending about 2 mm. past each end of the cathode; the glow then flashes suddenly round to the far side of the cathode (c), and there is an accompanying large increase of current. The lowest current which was obtained in these tests was about 0·3 milliamps; if the voltage drop reduced the current below this the glow was extinguished.

V. FORM OF THE CHARACTERISTIC.

Examination of the characteristic curve of the neon lamp, of which Fig. 3 is typical, shows that, starting with the largest currents, the graph is a straight line from the highest voltage used down to the point *A*. This part will be termed Region I. *A* is the last point at which the glow completely covers the cathode. At *A* the slope abruptly decreases, but the graph remains straight for further reduction of current down to somewhere about *B*; this is Region II. To the left of *B* Region III. shows, as the current falls, a slow decrease of the P.D. to a very flat minimum. Finally (Region IV.) the graph turns upward, the P.D. increases rapidly and almost linearly as the current falls, and approaches a definite value (for a given lamp) for vanishingly small currents. We interpret these results as follows:—

Region I. is that in which the current density is proportional to the current, since the cross-section of discharge is roughly constant. The cathode fall in this region depends on the excess of the current i above a critical value i_0 . Aston and Watson* find the cathode fall in such circumstances to be $V_0 + k(i - i_0)^{\frac{1}{2}}$, where k

* Proc. Roy. Soc. (A) 86, 168.

is a constant and V_0 is the constant value assumed for currents smaller than i_0 . This does not appear possible in the present case; the graph is very definitely straight, so that $V_0 + k(i - i_0)$ represents the cathode fall, and we may write $V = V_0 + k(i - i_0) + \beta i$, the last term representing a uniform gradient in the rest of the gap. From A to B (Region II.) the current density and cathode fall are constant and $V = V_0 + \beta i$. Region III. we take to be that in which the phenomenon of cathode fall becomes less marked. This brings us to Region IV., where, with practically uniform gradient, decrease in the current—i.e., in the number of negative ions available to produce others by collision—causes a greater and greater potential difference to be necessary to maintain the discharge. Finally, when the current is vanishingly small, we reach the sparking potential as required by the theory of

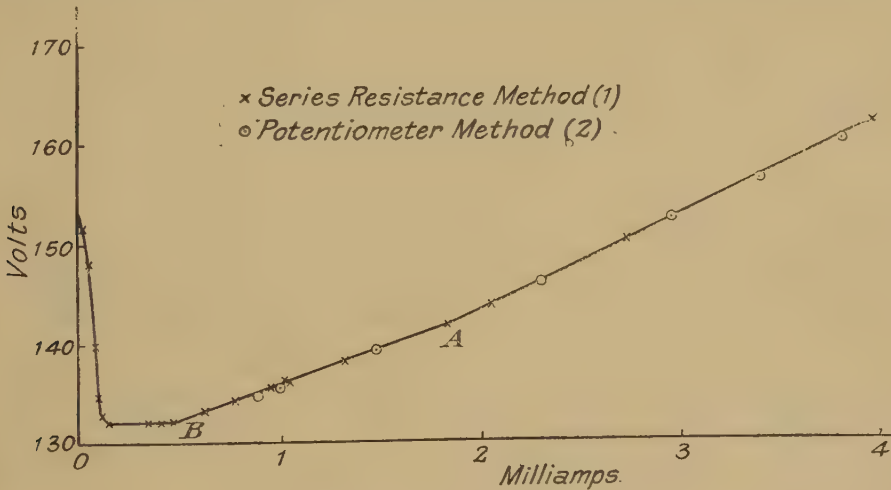


FIG. 3.—THE CHARACTERISTIC.

onization by collision.* This is clearly borne out by the tests; for the lamp illustrated and two others the figures run:—

Sparking voltage	153	149.5	161-165
Limiting voltage	153	150	163

The fact alluded to above that the current and P.D. only settle gradually to their final steady values after a change is made in the resistance of the circuit, and this in a quite definite way, may be explained somewhat as follows: Suppose the external resistance is reduced; then there is an immediate increase of current and of potential difference between the plates. This last drives more of the existing positive ions to the cathode, and so diminishes the space charge near the cathode, and consequently also the cathode fall. Gradually, however, the space charge re-establishes itself, the cathode fall rises to its former value and the current correspondingly drops until the current density recovers its normal measure. The immediate increase of potential fall across the electrodes is thus finally still further enhanced while the initial increase of current is lessened. This is what we have seen to be the case.

* Townsend, Ionization of Gases by Collision, p. 66.

VI. THE NEGATIVE PART OF THE CHARACTERISTIC.

The region of small currents is particularly interesting. Here the characteristic is markedly negative, increase of potential fall accompanying decrease of current. The form of the curve is somewhat as shown in Fig. 4, being convex upward in part of its length. Let E be the applied voltage, R the external resistance, and consider any point $P(V, i)$ on the curve. Join EP . Then $PM = V$, so $EN = E - V = Ri = R \cdot PN$. Thus the slope of the line EP is equal to R , the external resistance. Hence, if, as at P , the line EP meets the curve from the left-hand side, any slight decrease of the current will result in a decrease of the slope of EP —i.e., the current is such as should correspond to a smaller R . Hence, if R remains unchanged, the current will decrease still more; this part of the characteristic is unstable. This instability gives the necessary condition for the lamp to give an intermittent glow automatically, and without the separate shunting condenser which produces the Pearson-Anson flashing. The lamp itself possesses capacity, and in this unstable region the increase of P.D. associated with the charging up of

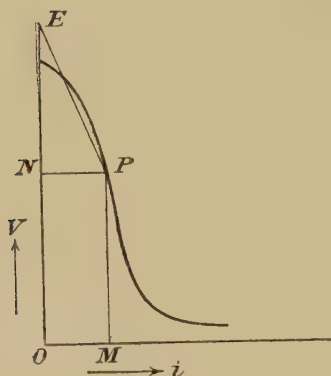


FIG. 4.

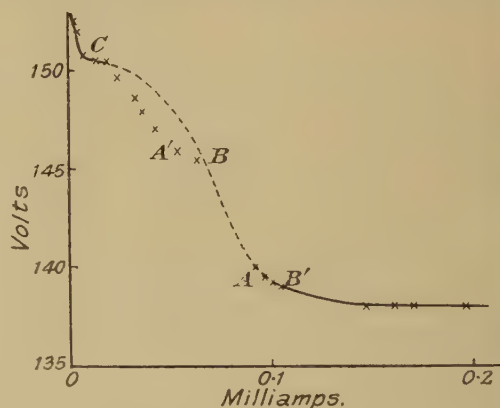


FIG. 5.

(Curve between B' and A continuous.)

this capacity goes with a diminished current, or, conversely, a rush of current will produce a drop of potential, which, if the fall is rapid enough, may bring the potential below that required to maintain the discharge. The lamp will then go out and the cycle will recommence. This intermittency is easily observed either by the telephone or by a revolving mirror. With the lowest resistance at which intermittence sets in the latter is not complete—i.e., the conditions are not definitely unstable. The note in the telephone is harsh, and the mirror shows great irregularity in period. If the external resistance is increased the periodicity becomes quite regular—i.e., the lamp goes out in every cycle. The note is now high and clear; with resistances of about a megohm or upwards the discharge only occupies a small fraction of the period, as is shown by the narrow bright lines separated by broad dark spaces seen in the rotating mirror. As we have pointed out, if the conditions at P are unstable, the line EP must meet the curve from below. The point at which intermittence sets in cannot be determined with sufficient exactness to prove the fact absolutely, but it appears to be about where the line EP is tangential to the curve, as the above theory requires.

Further, the form of the characteristic shows that, as the current is made smaller, a point should be reached at which the line EP meets the curve again from above, i.e., that the instability and the intermittence should cease. Actually, if the external resistance is steadily raised, this is found to be the case: the pitch of the note in the telephone falls gradually, and then, at a definite point, the discharge becomes continuous once more.

We have studied this part of the characteristic in greater detail. In Fig. 3, since the observed points on the negative branch of the curve are mostly in the intermittent region, it is clear that the voltage and current values attributed to them are merely time averages, depending on the periods and damping of the voltmeter and ammeter, as well as on the instantaneous values of the P.D. and current during the illuminated part of the cycle. We therefore determined with great care a number of points on the continuous parts of the graph, on both sides of the intermittent region. The result is shown in Fig. 5. Starting from the right-hand side, and increasing the resistance in series with the lamp, the graph is traced up to the point A . Intermittence then sets in, and point A' gives the corresponding readings of the voltmeter and ammeter. Still increasing the resistance, the succeeding separately plotted points are recorded, and then, about the position of the "kink" at C in the curve, the current becomes continuous again. Reversing the process, i.e., with decreasing resistance, the separate points representing the intermittent region can be got down as far as B , where the current becomes continuous again and the characteristic leaps to B' , whence it proceeds as before towards the right.

The actual form of the graph between A and C , i.e., the true values of the P.D. and current during the brief conducting part of each cycle, cannot be determined. But the position at which the curve turns upward, before intermittence sets in, does not seem compatible with a single sweep from the part $B'A$ joining up to the final continuous part with the smallest currents. Further, the "kink" shows a much-flattened portion; even if the current is not quite continuous along all this flattened part, still the proportion of the time of current-flow to that of darkness is increasing, and in such circumstances the readings approximate to their positions on a true characteristic curve. For these reasons it appears probable that the true characteristic would have a form something like that shown by the dotted curve. While we were unable to make any exact allowance for the voltmeter and ammeter, experiments with a commutator show that the latter reads proportionately much lower than the former with intermittent currents.

VII. ALTERNATING CURRENT PHENOMENA.

A peculiar phenomenon is seen if the lamp is run with alternating current at 200 volts and viewed by reflection in a rotating mirror. The glow is, of course, intermittent with twice the periodicity of the supply, since current passes only when the supplied P.D. has risen to the sparking potential (V_A) and ceases as soon as it falls below the potential (V_B) required to maintain discharge. But, further, the glow thus produced round about the crest of each half-cycle is not simple, but is itself broken into four bright patches separated by dark intervals. If the voltage of the supply is gradually cut down the first and the last of the bright patches become dimmer, and they eventually disappear, the first being the first to go. With further

diminution the remaining pair weaken and vanish in a similar way. It is clear that the applied P.D. cannot be less than V_B during these dark intervals, so the suggestion arises that when the sparking potential V_A is reached the resulting rush of current causes such drop of potential through the gas that the discharge can no longer be maintained. If this be so the same thing should occur also just after the switching on of direct current to the lamp. It is not possible to verify this with the rotating mirror, because one cannot view the exact start of the current save by an unlikely chance. But if the current is supplied through a rotating make-and-break commutator, with or without reversal, the phenomenon is at once apparent: the bright segments are cut across by dark gaps. The duration of the first flash appeared to be somewhat variable, but our apparatus was not such as to permit any measurement of its value. The current certainly flows for an appreciable time, for if the commutator bars are made narrow and the spaces wide, the short flashes which result are single. The mechanism by which the lamp thus "puts itself out" until a steady supply of ions has accumulated to carry the discharge is obscure, since in these experiments there is no large external resistance to take up the potential drop which seems to be thrown out by the lamp.

VIII. MEASUREMENT OF A.C. FREQUENCY.

The use of the rotating commutator in these experiments suggested a simple method of measuring the periodicity of an alternating current supply. On such a supply the electrodes of the lamp glow alternately, while on D.C., of course, only one glows. This fact is made use of by connecting the A.C. mains to a commutator driven by a small motor, the interrupted current being passed on to an Osgilby lamp. By adjusting the motor speed the current through the lamp can be made uni-directional, as shown by the fact that the glow remains on one electrode only. Our commutator made eight contacts per revolution and, by suitably connecting the mains and lamp, the current could be either interrupted only or interrupted and reversed. The motor speed was adjusted roughly, by means of a rheostat, to give the necessary frequency of interruption; with such adjustment the lamp electrodes glow alternately, but each remains glowing for an appreciable time, the longer the more nearly exact the speed. Final control is obtained by resting the hand lightly on the pulley of the commutator. In this way it is possible to keep the lamp glowing on one electrode for ample time to determine accurately the speed of revolution of the commutator. It is not essential to secure this condition, for if the speed is maintained alternately just above and just below the true speed for, say, two or three minutes, the required frequency is given with good accuracy by the quotient of the total number of revolutions by the time. The function of the lamp is to give a criterion for the adjustment of the speed, and this it does excellently.

There are, of course, a number of possible frequencies of revolution of the commutator, any of which gives uni-directional current through the lamp. If the current is interrupted only, the frequency may be any submultiple of the A.C. frequency N ; if it is interrupted and reversed, any submultiple of $2N$. Usually one knows roughly the value of N , but if not, runs at different speeds enable the true value of N to be found, since if one commutator speed is N/n (both N and n unknown), the next speed is $N/(n-1)$.

The following results illustrate the accuracy of the method :—

Current interrupted but not reversed—

No. of contacts	3,920	5,880	2,990
Time (sec.)	96.5	145	74
Contacts per second	40.6	40.5	40.4

∴ frequency of supply = 40.5.

Current interrupted and reversed—

No. of contacts	...	3,920	5,880	1,960	5,652
Time (sec.)	...	146.5	217	73.25	211
Contacts per second	...	26.8	27.1	26.8	26.8

∴ frequency of supply = $26.9 \times 3/2 = 40.3$.

DISCUSSION.

For Discussion see page 278.

XIV.—NOTES ON SOME ELECTRICAL PROPERTIES OF THE NEON LAMP.

By U. A. OSCHWALD, *B.A.*, and A. G. TARRANT, *B.Sc., A.R.C.S., F.Inst.P.*

Received October 23, 1923.

(Communicated by S. SKINNER, M.A.)

ABSTRACT.

These notes consist of selected portions of a more comprehensive survey, and therefore deal with three isolated problems only, viz.:

- (1) The wave form of an "oscillating" neon lamp.
- (2) The maximum frequency of an "oscillating" neon lamp.
- (3) The persistence of the ionisation in a neon lamp.

(1) By means of a special accurately timed switch, a neon lamp was thrown into the "oscillating" state, and its voltage measured after any predetermined interval (from 0.005 to 0.5 seconds). Thus the voltage-time curve of the "oscillating" lamp was plotted. Very close agreement with theory is found.

(2) A neon lamp was made to oscillate at its highest possible frequency, which was measured by a tuned circuit. Measured frequencies did not agree well in this case with theory, but a maximum frequency of about 95,000 is observed.

(3) A neon lamp was run at such a voltage that if the discharge were interrupted for any considerable time it would not restart, the voltage being below the minimum starting voltage for the lamp. The circuit was interrupted by a special high-speed interrupter for separate single intervals down to 5×10^{-5} seconds. In no case did the discharge restart, showing an ionisation persistence of less than this interval.

IN connection with certain experiments on the neon lamp it became a matter of interest to the authors to investigate the behaviour of the lamp rather fully. While much of the ground covered by these experiments has been already the subject of research by other workers, and has been referred to in other Papers to this Society, in one or two points the methods used by the authors are believed to be sufficiently novel to be of interest.

The authors have, therefore, included in this brief note only these points, with as brief a preface as is possible.

The points dealt with in this Paper are:—

1. The experimental determination of the wave form of the "oscillations" of a neon lamp.
2. The maximum frequency obtainable with an "oscillating" neon lamp.
3. The maximum interval of interruption for a "steady" neon lamp.

EXPERIMENTAL VERIFICATION OF WAVE FORM.

To confirm the mathematical conclusions that have already been published as to the behaviour of the "oscillating" neon lamp, an experimental determination of wave form and frequency was carried out. An oscillation frequency of about three per second was used under such circumstances that certain disturbing factors

would be quite inappreciable. The result has confirmed the mathematical predictions very satisfactorily.

For this purpose the lamp was connected to the supply battery* through a high resistance, and the voltage maintained throughout at 180 volts. Under these circumstances the lamp discharge (having only the lamp self-capacity to cause oscillations) would be either non-oscillatory, or have an extremely high frequency.

By means of the special time switch described below a condenser of 1 microfarad capacity was then connected across the lamp. The lamp capacity being only 8 cm., and the resistance of the leads negligibly small compared with the high resistance in the supply circuit, the first effect was to cause the lamp voltage to fall almost to zero. The lamp and condenser then became charged up comparatively slowly, until the voltage became high enough for the lamp-discharge to start. When this point was reached the voltage fell until the discharge ceased; the condenser

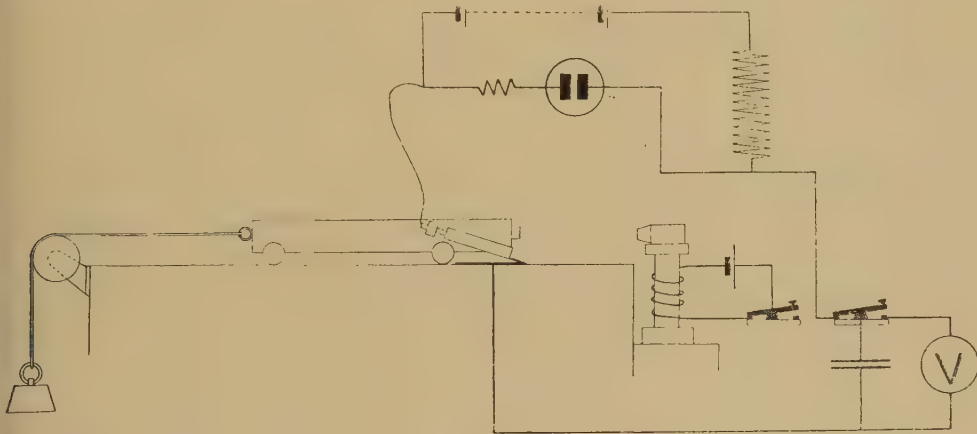


FIG. 1.

and lamp then became charged up again, as in the ordinary oscillatory state of the lamp.

By means of the time-switch the condenser was disconnected from the lamp after some specified and known time. At any instant, as the condenser and lamp were connected by leads of negligible resistance, the condenser voltage would be the same as the voltage across the lamp. At the instant of disconnection the condenser was

* In the whole of their investigations on the Neon lamp the authors have used a *high-tension battery* as a source of supply, and not a dynamo. Not only is it difficult to prevent accidental small voltage changes where dynamo-energised public supply mains are used, but the voltage of such mains is usually affected by more or less of a "ripple," due to small periodic variations of voltage. In the case of the public supply mains in the authors' laboratory, for instance, the nominal voltage is 200, but actually the value oscillates between 199 and 201, with a frequency of oscillation of 305 per second. Such variations are serious in dealing with the Neon lamp. A further advantage of a battery supply is that no large series resistances are necessary to regulate the voltage, and a further objection to a dynamo supply is that large and unknown inductances (in the dynamo) are included in the lamp circuit. For these reasons the authors regard the use of a battery supply as essential in this case.

therefore left charged up to a voltage equal to the lamp voltage at that instant. This condenser voltage was then measured on an electrostatic voltmeter.

The time-switch, whose function was to connect the condenser with the lamp for some accurately known time, consisted of a metal style attached to the prong of a tuning fork, which made contact with a triangular metal plate fastened to the bench. The tuning fork was carried by a heavy trolley, which was dragged along

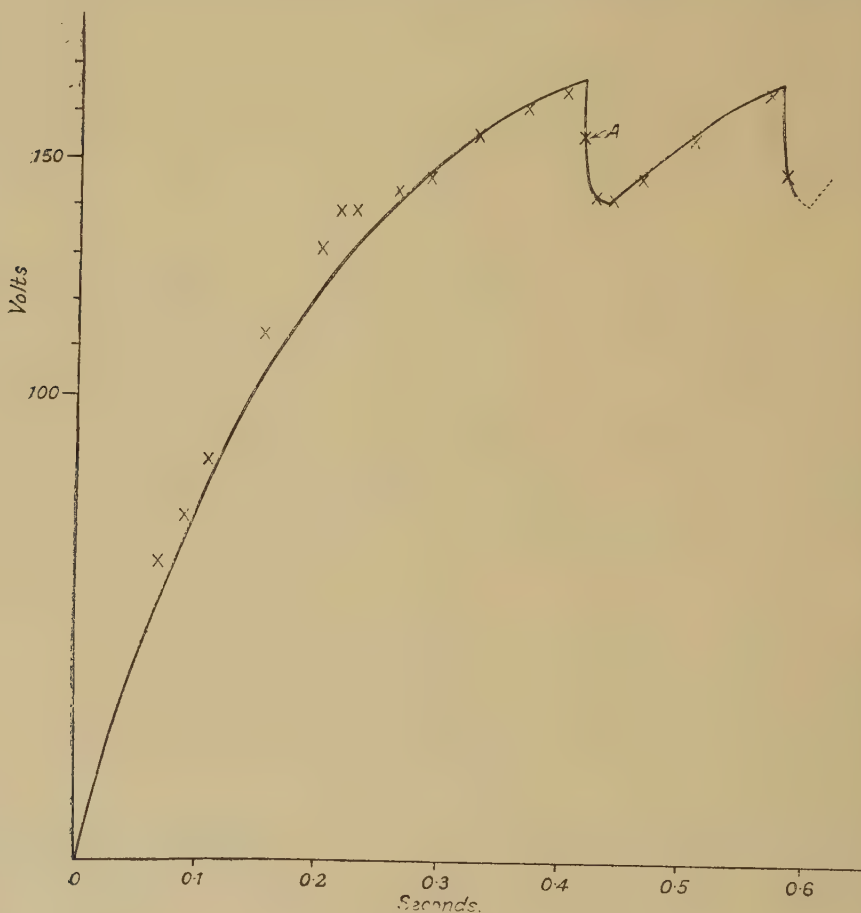


FIG. 2.

the bench by a cord which passed over a pulley and carried a heavy weight on its other end. The trolley was fitted with an electromagnetic release.

The plate on which the style made contact was coated with soot from a candle flame, so that each passage of the style across it left a visible trace. If the tuning fork was vibrating, this trace was sinusoidal, and from the number of waves in the trace the actual time of contact could be conveniently and accurately found. The general arrangement is shown diagrammatically in Fig. 1.

In carrying out any particular determination with this apparatus, the trolley

was arranged so that the time of contact (as estimated from the trolley speed and the part of the plate across which the style would travel) would be approximately that required for the particular test being carried out ; the lamp was switched on (without the condenser, of course), the condenser discharged so as to be sure of its having no initial voltage, the fork bowed, and the electromagnetic release key pressed.

The trolley then ran along the bench, dragging the fork with it, so that the style made contact with the plate for the desired time. After contact had been made and broken, the voltage of the condenser was measured, and the time of contact found accurately from the fork trace. By means of a number of such runs, with contact times varying from 0.06 sec. to 0.6 sec., the voltages reached by the lamp and condenser in a large number of different times from start were found. These voltages, plotted against time of contact, gave the voltage-time curve of the oscillating lamp.

The results obtained are shown in Fig. 2, in which the observed points are shown by crosses. The curve is that mathematically predicted for these conditions.

The point *A* is of special interest, as at this point the time switch broke the condenser circuit during the lamp-discharge, the condenser being then left partly discharged.

The discrepancies observable at low voltages are probably due to irregular behaviour of the electrostatic voltmeter at these voltages. The very close agreement with the predicted curve over the oscillation range of voltage must be regarded as very satisfactory, having regard to the nature of the experiment. There is a slight systematic divergence, noticeable especially at the peaks of the curve, but the very regular and small divergence shows how closely the mathematical expressions quoted fit the results obtained in practice.

LIMITING CONDITIONS FOR LAMP OSCILLATION.

Voltage.

The starting voltage of the lamp varies with certain external conditions (which form the subject of another Paper by the authors), but under usual circumstances is about 164 volts for slow oscillations. For very rapid oscillations it is possible that this value may not apply, but on this point the experimental evidence is not conclusive.

Frequency.

The frequency has no lower limit—frequencies of the order of 1 discharge in 300 secs. have been observed. The upper limit is affected by many conditions, the highest value measured by the authors being 95,000, the limit lying apparently just above that figure. At very high frequencies the inclusion of inductances in the circuit have an obvious effect in maintaining oscillations above the limit otherwise obtainable.

It must be pointed out that the lamp currents at high frequencies are extremely small, so that the lamp is not a practical method of generating oscillations for radio transmission. The investigation of the current is, moreover, impossible by means of the ordinary oscillograph even at low frequencies.

The method used by the authors to investigate these frequencies was to include in the circuit of the lamp a coil which either formed part of or was coupled magnetically with part of a tuned circuit. Resonance in the tuned circuit was indicated

by the readings of a galvanometer which was energised from the resonating circuit through a crystal rectifier. The method, diagrammatically represented in Fig. 3, proved very satisfactory in use.

The results obtained, however, do not show an altogether satisfactory agreement with those theoretically deduced, and there is no doubt that the presence of tuned circuits coupled to the lamp circuit produces an illegitimate disturbance,* and it is also certain that the laws of lamp resistance, &c., deduced from observations on the "steady" lamp do not apply when the lamp is undergoing rapid oscillation.

MAXIMUM INTERRUPTION INTERVAL (CONTINUOUS DISCHARGE).

If the lamp discharge is progressing steadily, and the supply circuit is broken, the discharge, of course, instantly ceases. When the circuit is made again, if the voltage is above about 164 volts (under ordinary circumstances) the discharge starts. If the voltage is between 142 and 164 volts, the discharge will not start, though, if once started by a momentary raising of voltage it will continue when once started. This may be explained by supposing that on breaking the circuit the lamp reverts to a state in which any voltage above 164 will cause progressive self-ionisation to

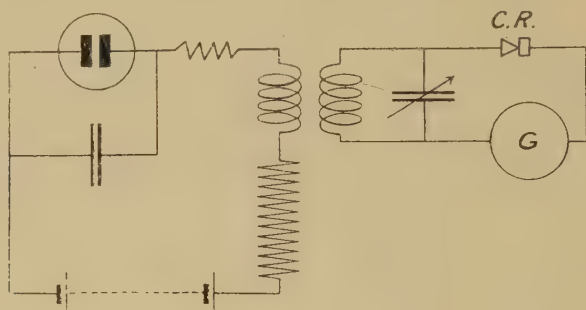


FIG. 3.

take place, and hence a current to be passed, while any voltage below that value will only cause ionisation to be maintained if it is already started.

Whether this reversion takes place instantly or not is a matter of some interest. The authors investigated this point by arranging a mechanical interrupter whereby the circuit could be broken only for a very small interval of time. If, then, the reversion of the lamp took any appreciable time, the circuit would be completed again before the lamp had become de-ionised, and the discharge would then start again even at voltages below 164.

The interrupter was made of two brass discs mounted on the axle of a small synchronous motor. Connection was made to each disc through two brushes, one making contact on the flat side and one on the edge of each disc. A small portion of the edge of each disc was cut away and replaced by ebonite, so that connection between the two brushes was interrupted while the peripheral brush rested on the insulating part of the disc. The two sets of brushes were connected in parallel, so that connection through the discs was only completely broken while *both* peripheral

* So far, the authors have been unable to find mathematical expressions even approximately applicable to this case.

brushes were in contact with insulating portions of their discs. By adjusting the relative positions of the discs on the axle (one being capable of being rotated round the axle, and locked in any desired position relative to the other) it was possible to arrange that one brush left the insulating portion of its disc almost at the same instant that the other brush entered upon the insulating portion. That is, one brush would close its circuit almost at the same instant that the other broke the circuit through the other disc, so that the total time of complete interruption of the circuit could be made very small.

The arrangement is shown diagrammatically in Fig. 4, in which, for the sake of clearness, the two discs are shown side by side instead of on the same axle.

A separate mechanical switch was arranged to short-circuit the disc interrupter, and only to include it in circuit for the time of one revolution of the discs, if required.

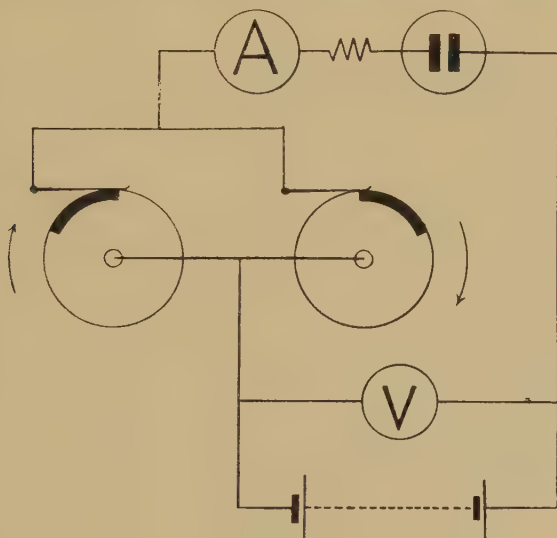


FIG. 4.

So that the lamp circuit could be kept closed for a long time, then broken once for a very short time by the disc interrupter, and then closed again for as long as required.

The time of interruption was determined electrically,* the shortest time used being 5×10^{-5} secs.

Under these circumstances a single interruption was sufficient to cause instant extinction of the discharge even at voltages only very slightly below the critical starting voltage. So that it may be concluded that, whatever actual time is taken for the de-ionisation of the lamp, it is certainly below 5×10^{-5} secs.

* The method used for measuring the duration of circuit interruption may be of interest. The auxiliary mechanical switch was kept open, so that the disc interrupter broke circuit once per revolution. It was then used to complete a galvanometer shunt circuit, and from the galvanometer readings it was possible to calculate for what fraction of each revolution the disc circuit was broken. Measurements were made at various disc speeds, and the interrupter was found very consistent in its behaviour at all speeds. From a knowledge of the speed of the disc motor, and of the fractional interruption of the circuit, the actual time of interruption was calculated.

The actual figures obtained in one test, for instance, showed that the circuit was broken for 1.09 thousandths of each revolution. The discs speed being 1,280 revolutions per minute, the time of interruption was 5.23×10^{-5} secs.

In conclusion, the authors wish to express their thanks to the Governors and Principal of the Chelsea Polytechnic for the facilities accorded them for carrying out these experiments, and to their colleagues on the staff of that institution for certain useful suggestions made during the course of the research.

DISCUSSION.

For Discussion see page 278.

XV.—A CRITICAL RESISTANCE FOR FLASHING OF THE LOW VOLTAGE NEON DISCHARGE TUBE.

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Received January 30, 1924.

(Communicated by Prof. G. W. TODD.)

ABSTRACT.

The Paper deals with the resistance conditions necessary for the maintenance of the well-known phenomenon of "flashing" of the neon discharge tube. It is shown theoretically that there is a critical value R_c , for the resistance in series with the neon tube, below which no flashes can be obtained.

This critical value of the resistance is expressed by the relation $R_c = \frac{E - V_B}{k(V_B - V_A)}$ where E is the charging voltage, V_B the lower critical voltage, V_A the kathode fall of potential (approximately), and k the conductance of the discharge tube.

Experimental observations confirm this relation exactly in the case of the "Osglim" lamp.

THE lamps used in these experiments were of the "Osglim" type, and consist of two electrodes of pure iron, the kathode being of large area and in the shape of some letter of the alphabet, whilst the anode is a small cylinder separated from the kathode by a distance of a few mm.s. The contained gas is a mixture of 75 per cent. of neon, and 25 per cent. of helium at a pressure of approximately 10 mm.s of mercury.

The ballasting resistances usually contained in the caps of the lamps were removed.

INTRODUCTION.

The phenomenon of "flashing" of the lamps is well known (see "The Neon Tube as a Means of Producing Intermittent Currents," by S. O. Pearson, *B.Sc.*, and H. St. G. Anson. Vol. 34, p. 204, Proc. Phys. Soc., Lond.).

If a high-resistance R is connected in series with a neon lamp, having a capacity C shunted across its electrodes (Fig. 1), the continuity of the current through the lamp is interrupted, and it "flashes" at regular intervals of time. The time T between flashes is equal to the time required for the condenser to charge up added to the time necessary for it to discharge through the lamp.

The equation for T , the time of flash, was first obtained by Anson and Pearson (loc. cit.). In this determination they obtained the current-voltage law for the lamp empirically from a consideration of the graphs between these quantities.

A similar relation has been obtained by one of us* theoretically on certain

* See Journal of Scientific Instruments. "The Application of the Neon Lamp to the Comparison of Capacities and High Resistances." J. Taylor and W. Clarkson. Vol. 1, No. 6, March (1924).

assumptions, of the form

$$i = k(V - V_A) \quad \dots \dots \dots (1)$$

where i = the current through the lamp, in microamperes.

V = the voltage across the lamp electrodes, in volts.

V_A = the kathode fall of potential (approximately) in volts.

k is a constant depending on the area of the kathode utilised during the discharge, and may be termed the conductance of the lamp.

To start the discharge a voltage V_c , termed the higher critical voltage, greater than that required to sustain the discharge is required.

The voltage necessary to maintain the discharge after it has once started is termed the lower critical voltage V_B ($V_B < V_c$).

C , the condenser which is shunted across the lamp electrodes (Fig. 1), charges

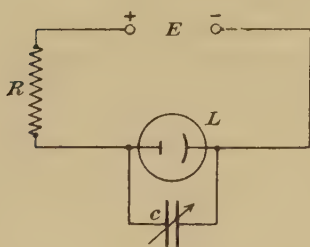


FIG. 1.

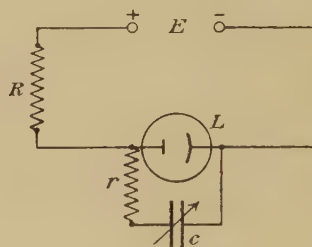


FIG. 2.

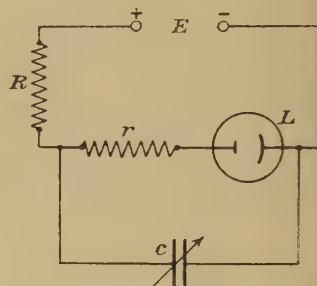


Fig. 3.

up, and discharges through the lamp, between the voltages V_B and V_c . The time T for the total period is evidently given by

$$T = t_1 + t_2,$$

where t_1 = the time in secs. for the condenser to charge up.

t_2 = the time in secs. for the condenser to discharge through the lamp.

t_1 is given by the usual formula.

$$t_1 = CR \log_e \frac{E - V_B}{E - V_c} \quad \dots \dots \dots (2)$$

where E = voltage of the charging battery.

C = the capacity of the condenser in microfarads.

R = the resistance in series with the lamp (Fig. 1) in megohms.

As soon as the condenser has charged up to a potential of V_c volts, discharge through the neon-tube begins. Simultaneously, however, the condenser is charging up through the series resistance R , from the source of voltage E .

From equation (1) the quantity of electricity dq passing through the lamp in dt secs. is

$$dq = k(V - V_A)dt.$$

In the same time a quantity of electricity $\frac{E - V}{R}dt$ flows into the condenser from the battery.

The net change of the condenser charge is therefore given by

$$-dq = \left[k(V - V_A) - \frac{E - V}{R} \right] dt \quad (3)$$

and solving this equation we obtain

$$t_2 = \frac{CR}{kR+1} \log_e \frac{V_c - \frac{E+kRV_A}{kR+1}}{V_B - \frac{E+kRV_A}{kR+1}} \quad (4)$$

THE CRITICAL RESISTANCE FOR "FLASHING."

From general considerations it is obvious that there should be some limiting value R_c for the resistance in series with the lamp, below which "flashes" are impossible: this condition is expressed physically by the fact that during any instant of the discharge through the lamp, the quantity flowing from the condenser is exactly balanced by the quantity which flows into the condenser from the charging battery.

This condition is evidently from equation (3) expressed by the relation

$$\frac{E - V}{R} = k(V - V_A) \quad (5)$$

If $\frac{E - V}{R} > k(V - V_A)$, no "flashes" are possible and a steady discharge ensues.

Now V may have any value between V_c , the higher critical voltage and V_B , the lower critical voltage; consequently the maximum value for R (i.e., R_c) for which there is no "flashing" is given by

$$\frac{E - V_B}{R_c} = k(V_B - V_A)$$

or

$$R_c = \frac{E - V_B}{k(V_B - V_A)} \quad (6)$$

R_c is therefore a linear function of E , for a constant value of k the conductance of the lamp. For values of C of 0.1 microfarads upwards, k is almost constant for different capacities, hence R_c should be independent of C for such values of the capacity.

With small capacities, k diminishes owing to the very small electrode area utilised during the luminous period, and consequently R_c should increase as C decreases, for low capacities.

Further, since k is different, if we commence with $R < R_c$, which corresponds to a steady discharge, and then increase R , R_c for increasing resistance should be different from and greater than R_c for decreasing R .

In actual practice with condensers of 0.1 microfarads upwards, and battery voltages ranging from about 180 to 260 volts, it is found that conditions are neither definite nor repeatable, because the current through the lamp at the critical resistance is too great, and consequently the neon tube is working under more or less unstable conditions.

There are two methods, the same in principle, by which R_c may be elevated to a suitable value so that readings are repeatable to within one or two per cent.

Resistances r are introduced into the condenser circuit, so that the resistance through which discharge occurs during the luminous period is elevated. Moreover by this method the area of the kathode utilised during discharge is progressively diminished as r is increased, so that the conductance k of the lamp is lowered in value. The alternative positions of the resistance r are shown diagrammatically in Figs. 2 and 3.

THE GENERAL PROBLEM OF THE CRITICAL RESISTANCE FOR "FLASHING" OF THE NEON LAMP.

Let r_0 and r_1 be the resistances included in the circuit as shown in Fig. 4.

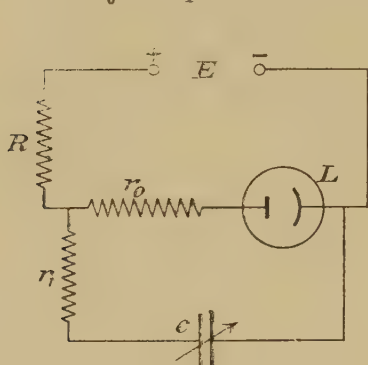


FIG. 4.

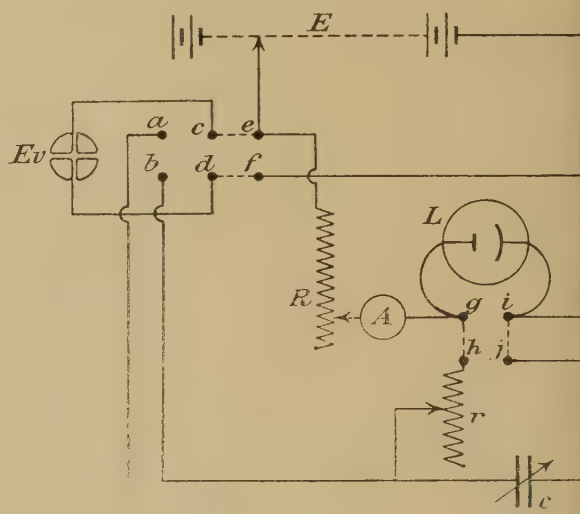


FIG. 5.

Let V_0 = the potential across the lamp electrodes at any instant.

V = the potential fall across r_0 and the lamp electrodes.

V' = the potential across the condenser C .

Then at any instant of the discharge from the condenser through the lamp, we obviously have

$$\frac{E-V}{R} + \frac{V'-V}{r_1} = \frac{V-V_0}{r_0} \quad \dots \dots \dots (6)$$

and

$$\frac{V-V_0}{r_0} = k(V_0 - V_A) \quad \dots \dots \dots (7)$$

Also considering the net loss of condenser charge dq in the time dt secs. we have

$$-dq = \frac{V'-V}{r_1} dt \quad \dots \dots \dots (8)$$

and substituting for V' in equation (8) from equation (6)

$$-dq = \left[\frac{V-V_0}{r_0} - \frac{E-V}{R} \right] dt. \quad \dots \dots \dots (8)^1$$

As before the condition that no "flashing" shall occur is given by the relation $-dq=0$, and therefore the discharge is steady when

$$\frac{E-V}{R} \geq \frac{V-V_0}{r_0} \quad (9)$$

introducing into equation (9) the value of $\frac{V-V_0}{r_0}$ obtained from (7)

$$\frac{E-[kr_0(V_0-V_A)+V_0]}{R} \geq k(V_0-V_A). \quad (9)^1$$

The values for V_0 are confined between the higher and lower critical voltages,

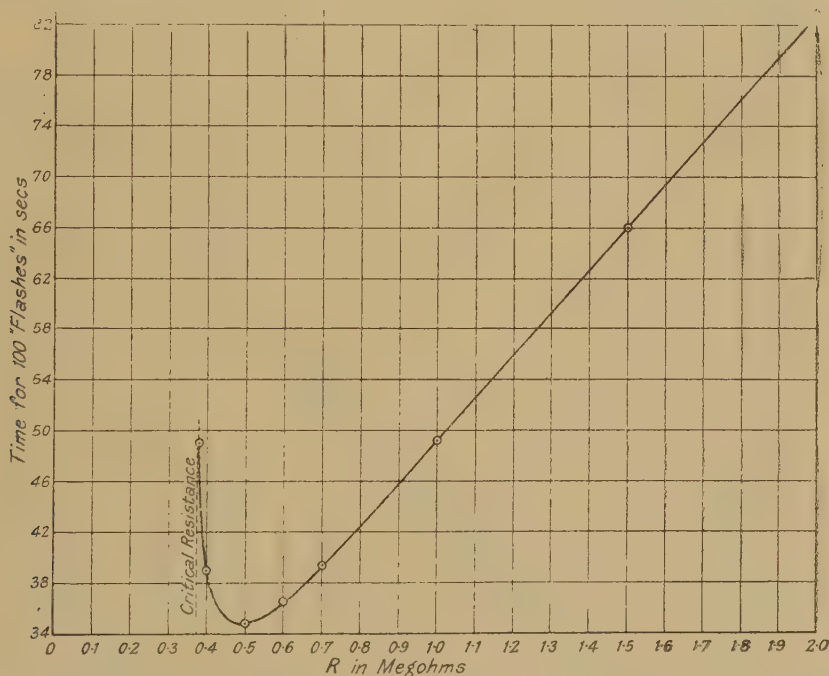


FIG. 6.—GRAPH SHOWING THE GENERAL FORM OF THE CURVES OF THE RELATIONSHIP BETWEEN THE TIME OF "FLASHING" T AND THE CIRCUIT RESISTANCE R .

so that the largest value of R fulfilling the conditions of equation (9)¹ is given for $V_0=V_B$. If R_c is this critical value of the resistance we have

$$\frac{E-[kr_0(V_B-V_A)+V_B]}{R_c} = k(V_B-V_A) \quad (9)^2$$

with $r_0=0$ (9)² becomes

$$\frac{E-V_B}{R_c} = k(V_B-V_A) \quad (9)^3$$

an exactly similar form to that previously obtained (see equation (5)).

With $r_0>0$ we have

$$E-kr_0(V_B-V_A)-V_B=kR_c(V_B-V_A)$$

$$\text{whence} \quad \frac{E-V_B}{R_c+r_0} = k(V_B-V_A) \quad (9)^4$$

The theory applies to a change from "flashing" to steady discharge, so that in obtaining the critical resistance R_c , R must be adjusted from higher to lower values, beginning with values well above the critical one.

THE EXPERIMENTAL METHOD AND RESULTS.

The diagrammatic representation of the circuit employed in the experiments is shown in Fig. 5.

E is the charging battery, of variable voltage.

L the neon lamp.

C the variable capacity across the lamp electrodes.

R the variable series resistance.

r is the resistance in the condenser circuit (variable).

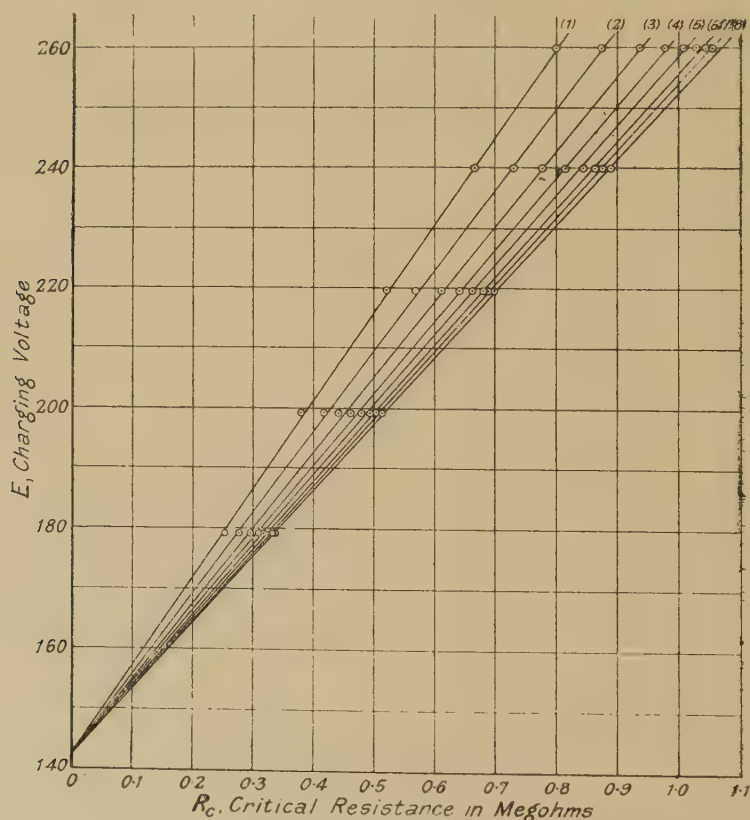


FIG. 7.—GRAPHS SHOWING THE RELATION BETWEEN THE CHARGING VOLTAGE E AND THE CRITICAL RESISTANCE R_c FOR DIFFERENT VALUES OF THE CONDENSER CIRCUIT RESISTANCE r (FIG. 2).

In Graph (1) $r=0.01$ Megohms.

" " (2) $r=0.02$ "

" " (3) $r=0.03$ "

" " (4) $r=0.04$ "

In Graph (5) $r=0.05$ Megohms.

" " (6) $r=0.06$ "

" " (7) $r=0.07$ "

" " (8) $r=0.08$ "

GENERAL FORM OF GRAPHS $\frac{E - V_B}{R_c} = \text{CONST.}$

E.v. an electrostatic voltmeter, *A* a micro-ammeter, *a.b.c.d.e.f.* a double-pole-double-throw switch, so that either *E* or the voltage across *C* may be measured, and *g.h.i.j.* a double-pole-single-throw switch so that *C* may be disconnected from across the lamp electrodes.

In the actual experiments the current through the lamp at the critical resistance, and the voltage across the condenser *C*, were measured. The critical point is very distinct. The graph of Fig. 6 indicates the general form of the graphs showing

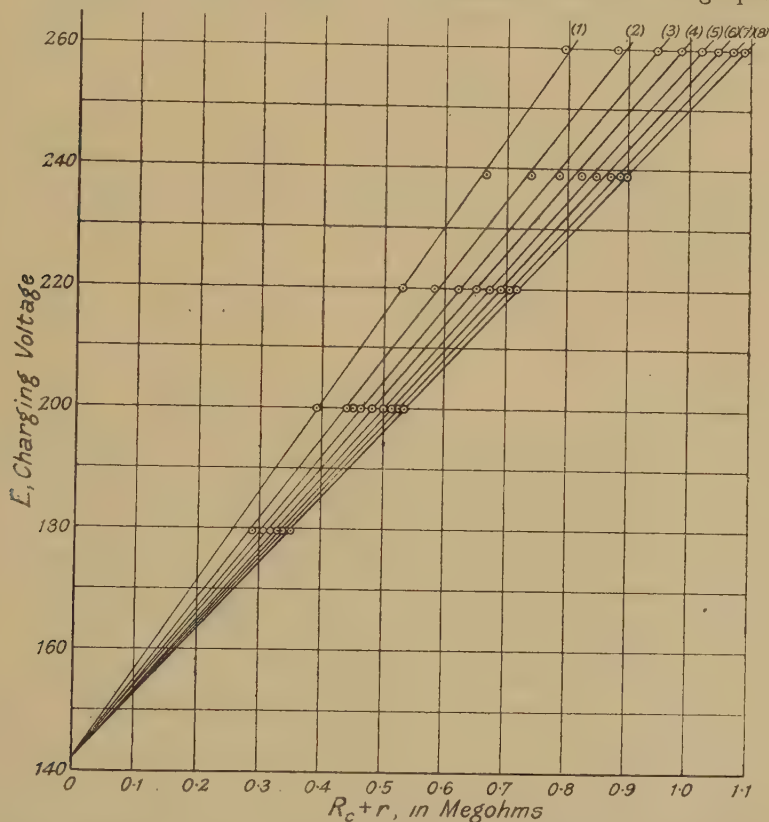


FIG. 8.—GRAPHS SHOWING THE RELATIONSHIP BETWEEN THE CHARGING VOLTAGE *E* AND THE CRITICAL RESISTANCE ($R_c + r$) FOR DIFFERENT VALUES OF THE CONDENSER CIRCUIT RESISTANCE r (FIG. 3).

In Graph (1)	$r = 0.01$	Megohms.	In Graph (5)	$r = 0.05$	Megohms.
" " (2)	$r = 0.02$	"	" " (6)	$r = 0.06$	"
" " (3)	$r = 0.03$	"	" " (7)	$r = 0.07$	"
" " (4)	$r = 0.04$	"	" " (8)	$r = 0.08$	"

GENERAL FORM OF GRAPHS
$$\frac{E - V_B}{R_c + r} = \text{CONST.}$$

relationship between the time of "flashing" *T* and the circuit resistance *R*; in the neighbourhood of the critical resistance the time of "flash" increases very rapidly with decrease of *R*, so that the curve rises almost vertically to an infinite value of *T*, which corresponds to a steady discharge.

The curves of Fig. 7 show the relationship between the critical resistance R_c (in megohms) and the charging voltage E for different values of r in the position shown in Fig. 2. These all prove to be linear functions which are seen to intersect the voltage axis at a common point the ordinate of which has the lower critical voltage value for the lamp.

In all the lamps experimented with, it was found by actual measurement that the voltage across the condenser (with the circuit of Fig. 2) at the critical resistance fell to the lower critical value V_B .

The general form of the graphs is

$$\frac{E - V_B}{R_c} = \text{const.} = D \quad \dots \dots \dots (10)$$

where D is dependent on r alone and is approximately the same as the current through the lamp at the critical resistance.

Fig. 8 gives the curves for the circuit represented in Fig. 3; the curves are linear and of the form

$$\frac{E}{R_c + r} = D \quad \dots \dots \dots (10)^1$$

D , as in the previous curves [equation (10)], varying with r , because of the dependence of k on r .

The experimentally obtained relations (10) and (10)¹ are seen to be in accordance with the theoretical relations of (9)³ and (9)⁴, and we have that $D = k(V_B - V_A)$.

The constant D (for both circuits) increased with decrease of r , but proved to be constant within the limits of experimental error for a fixed value of r between the limits of the charging voltages E (180 to 260 volts) which were employed. D , which, of course, represents the slopes of the graphs in Figs. 7 and 8, proved to be approximately equal to the current through the lamp at the critical resistance. R_c is constant and independent of the charging voltage E .

If R was stepped up from lower to higher values the critical resistance was found in accordance with the theory to be much greater than that for decreasing values of R .

It would appear that, so far as the critical resistance is concerned, r functions solely in regulating the effective conductance of the lamp. Fig. 9 shows the graphs for the variation of D (the critical resistance current approximately) with r for the two circuits of Figs. 2 and 3.

The general form of the curves is

$$D = \frac{A}{r + B} + D_\infty \quad \dots \dots \dots (11)$$

and since $D = k(V_B - V_A)$, we may write

$$k(V_B - V_A) = \frac{A}{r + B} + k_\infty(V_B - V_A),$$

if we write $D_\infty = k_\infty(V_B - V_A)$.

Also putting

$$\frac{A}{V_B - V_A} = A_1$$

we obtain the relation

$$k = \frac{A_1}{r+B} + k_\infty \quad (11)^1$$

This relation is, of course, purely empirical, but it suggests in the case of the circuit of Fig. 2 that the conductivity is comprised of two parts, the one part k_∞ which would be the conductivity of the lamp if $r = \infty$, that is, if C were removed entirely; the other part attributable to the effect of the condenser- r -resistance circuit in regulating the quantity of electricity thrown through the lamp during discharge;

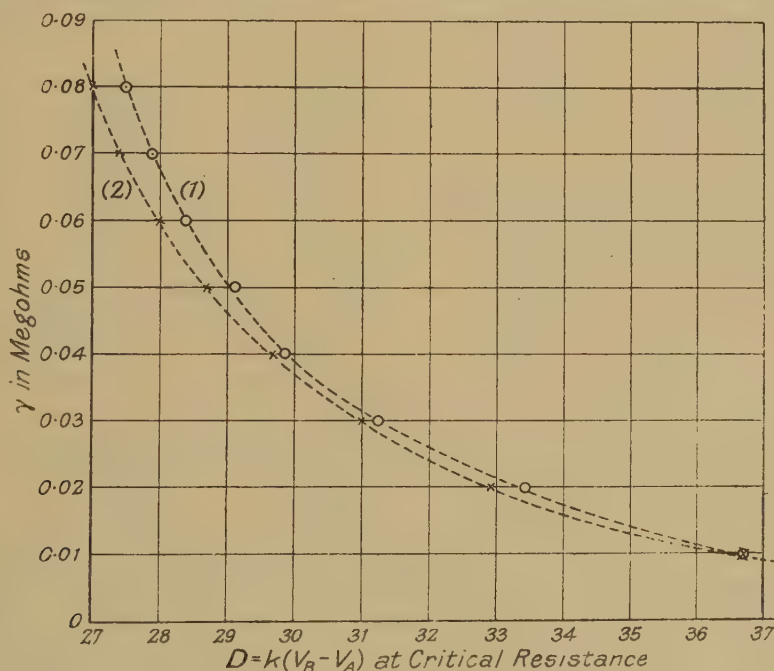


FIG. 9.—GRAPHS SHOWING THE RELATIONSHIP BETWEEN $D = [k(V_B - V_A)]$, AND THE RESISTANCE r FOR THE CIRCUITS OF FIGS. 2 AND 3.

Graph (1) is for Circuit of Fig. 2. Graph (2) is for Circuit of Fig. 3.

$$\text{GENERAL FORM OF GRAPHS IS } D = \frac{A}{r+B} + D_\infty$$

this suggestion is, however, not at all obvious in the case of the circuit of Fig. 3, for, with $r = \infty$, no current could flow through the lamp at all. k is, of course, dependent on the area of the cathode surface employed during discharge, and the area visibly decreases as r is increased.

For capacities of from 0.2 to 4 microfarads it was found that R_c was independent of C to within 1 or 2 per cent., but when the capacity C became small, the conductance

of the lamp diminished owing to the small energy transference during the luminous period. As C was decreased the value of R_c increased.

The following example illustrates the point :—

r Megohms.	R_c Megohms.	C Microfarads.
0.01	0.22—0.23	0.5
0.01	0.32—0.33	0.001
0.01	0.39—0.40	0.0005

It should be noted here that with some lamps it was sometimes possible to obtain flashing down to very low values of R , and the flashes were much more intense than was usual (since R was small); the condition, however, appears to be unstable and never lasted for a long period of time.

A further remark on the influence of magnetic fields on the critical resistance may be appended. A magnetic field transverse to the current direction in the lamp altered and lowered the critical resistance so that a continuous discharge gave place to a discontinuous one when the magnetic field was put on. A longitudinal field appeared to have very little influence on the critical resistance.

The electrodes of the lamps employed were of iron, consequently their shielding action from the field must be very considerable.*

We wish to acknowledge here our indebtedness to Prof. G. W. Todd, of Armstrong College, under whose supervision the experiments were carried out, and to the Department of Scientific and Industrial Research for the grant which has enabled one of us to undertake the work.

DISCUSSION on Papers XIII., XIV., and XV.

Mr. H. ST. G. ANSON mentioned that intermittence could be produced by a totally different method, viz., by putting the lamp in a magnetic field and in series with a resistance. The frequency of the intermittence depends both on the field and on the series resistance. As this result can be obtained with fields as small as that of the earth, it may account for some irregularities in repetition experiments.

Mr. J. W. RYDE: There are a few points that I should like to raise in connection with Messrs. Shaxby and Evans' Paper. Referring to the paragraph at the bottom of p. 257: their explanation of the fact that the current and potential take some time to reach steady values seems to be quite incorrect. In the first place, the space charge near the cathode is a *positive* space charge, and "... driving more of the existing positive ions to the cathode ..." will *increase*, not decrease it. Then in the last five lines of the same paragraph the authors say, "Gradually, however, the space charge re-establishes itself ..." Now it is well known that the time for the space charge to establish is of the order of a millionth of a second, so it is difficult to see how this can for a moment be accepted as an explanation of the time required to steady up.

I believe that the generally accepted explanation of this time effect is that it is due to—

- (1) Changes in the amounts of impurities present in the gas which produce relatively enormous effects on the characteristics.
- (2) Changes in or formation of adsorbed gas layers on the surface of the cathode.
- (3) Changes in the charges on the glass walls of the bulb and insulating supports.

The action of these effects on running the ordinary glow lamps is in general to *increase* the cathode fall, and therefore the voltage across the tube, and to *decrease* the current. After some time they reach equilibrium values, depending on the current and the potential across the elec-

* Experiments more recent than the above have shown that in the case of air discharge tubes (with electrodes near together so that the positive column is absent) exactly similar relations are obtained for the critical resistance for "flashing," over a wide range of pressures.

trodes. The instantaneous values of the voltage and current correspond to the particular state of the lamp at the time, hence "steady value" characteristics give little information of fundamental importance. The state of the tube enters as a variable. Everyone knows that similar conditions apply to the taking of the characteristics of "soft" valves. These effects explain the facts that the characteristics depend on the previous history of the lamp.

Referring to the curve, Fig. 3, of the present Paper, which shows the I/V characteristic. If the authors had taken *snap* readings, or worked with a tube filled with pure gas, I think they would have found the part of the curve to the right would have been concave to the current axis, and more nearly that to be expected from Aston and Watson's equation.

The explanation of the observations on p. 256 that a sudden drop of the voltage to a value about 5 volts above the normal going out voltage results in the discharge stopping also immediately follows. The current-voltage characteristic of the ordinary Osgilby lamp if taken after running it for some little time is shifted up the voltage axis, so that the going out voltage in this condition is higher than it was before running. If it is shifted up more than, say, 5 volts (as it often is), then clearly the lamp will go out if the potential is suddenly lowered to 5 volts above the original "going out" value. If, however, the potential is very slowly lowered, the lamp has time to adjust itself to approximately its original condition, and it will not go out until the potential is roughly the first "going out" value.

Referring to section VI, on the negative part of the characteristic, the conditions for stability were first given by Kaufmann in 1900, and also in J. J. Thomson's "Conduction of Electricity through Gases," p. 583.

I think I should take this opportunity to point out that it is of very little use to make any fundamental investigation on a commercial article such as a glow discharge lamp. It is well known that during the manufacture impurities, notably hydrogen, are deliberately introduced in to the gas, and in large scale manufacture traces of other impurities naturally find their way in. Thus in various commercial glow lamps I have found traces of N_2 , CO, CO_2 , H_2O , O_2 and Hg vapour, in addition to the impurities deliberately introduced.

Fractions of 1 per cent. of some impurities will lower the starting potential by 50 volts, and others will raise it even more, and similarly affect the characteristic curves. The minute traces of the impurities I have just mentioned do not matter when the commercial glow lamp is used as a lamp, but they make it of very little value for research or gas discharges.

Mr. A. G. TARRANT, referring to the Paper by Taylor and Clarkson, said that the authors appeared in some cases to have used a condenser connected across the lamp and high resistance, a second high resistance being added in series with the whole arrangement. Were they aware that this arrangement could, in some circumstances, give rise to a truly oscillatory, or unstable, current? He noticed during their demonstration that the telephones in series with the lamp gave an audible note, in addition to the clicks due to flashing of the lamp. Was this due to the instability referred to?

Mr. J. TAYLOR said that in consequence of the high value of di/dV over part of the characteristic it was possible to obtain considerable amplification of accidental disturbances, such as dynamo hum, and he would attribute the telephone note to some such cause. Rectification is also made possible by the sharp bend in the characteristic, and wireless signals can consequently be detected by means of the lamp.

Mr. J. H. SHAXBY, in reply to discussion on Paper XIII. (communicated): Dr. D. Owen's suggestion that, on our theory, the point at which the lamp becomes unstable should be further to the right along the curve if the applied voltage is lowered below the sparking potential V_A is borne out by experiment. Thus for instance, for a lamp whose sparking voltage is 155 and whose minimum voltage is 143, if the applied potential difference is lowered to the voltages of line 1 below, and the resistance then increased, the lamp goes out for values of the current given in line 2:—

Volts	153	146	142
Milliamps.	0.47	0.093	0.101

It is to be noticed that in this case intermittence does not occur, since once the lamp has gone out it cannot re-light.

Mr. Ryde is correct in supposing that "snap" readings give a curved right-hand portion of our Fig. 3. As we state, we found that final steady values of current and potential difference are reproducible, and our purpose was to determine how far these values conform to the linear relations indicated in Pearson and Anson's original Paper and to what extent the behaviour of the

lamp follows from the known physical laws. The work was an *ad hoc* investigation of these interesting properties of a commercial article, and not in any way a general research on discharges through gases.

Mr. Ryde does not appear to have understood our remarks at the end of section 5. It is, we think, obvious that, as he says, the factor determining the current and potential difference at any moment is what one may call the chemical state of the tube at that moment. What we had in mind were the electrical changes which go on hand in hand with these chemical changes; decrease of resistance causes *immediate* increase in current and potential difference, accompanied by diminution of the space charge by some of its positive ions being driven into the cathode. In a pure gas it is true that the space charge appropriate to the new conditions would be established in an exceedingly short time, but in the impure gases of the lamp *gradual* chemical changes set in and result in a further readjustment of the space charge, as a result of which the current drops until the current density recovers its appropriate measure.

The theoretical discussion in Taylor and Clarkson's Paper is based on the equation $i = k(V - V_A)$ (1) (V_A here is approximately the cathode fall), which expresses the linearity of the lamp characteristic over the range considered—i. e., between the sparking potential and the potential at which the lamp goes out when flashing. Equation (4) of Taylor and Clarkson's Paper is given in Pearson and Anson's Paper, and was also deduced by a rather different method by one of us (J. C. Evans) in our earlier work on the lamp. Its applicability is, of course, strictly confined to the straight line part of the characteristic. Taylor and Clarkson's readings for their graphs of Figs. 7 and 8 are for applied voltages between 260 and 180—viz., in the linear region to the right of point *A* in our Fig. 3. The agreement of the intersection points of these graphs with the value of the lower critical voltage V_R as found by experiment indicates that the point at which the lamp goes out in such experiments does not lie far to the left of our point *A*. This is borne out by our observations that a sudden drop of voltage causes the lamp current to fail at values much above those reached by a slow decrease of voltage (*see* table in paragraph IV of our Paper). It is clearly shown in Fig. 2 of Oschwald and Tarrant's second Paper that the drop in voltage during flashing occupies only about 1/40th second.

All the Papers read have confirmed the curious partiality of the lamp for linear relations, to which we have referred. This appears to be true both for the rapidly changing conditions which obtain in flashing and equally when the lamp is given time to settle down to a steady state as in our observations.

Mr. A. G. TARRANT (in reply to discussion): We note with much interest the results obtained by Messrs. Taylor and Clarkson, as during the preliminary part of our research we had also examined briefly the critical conditions for flashing of the neon lamp, and had obtained very similar results.

At the same time, we would hesitate to claim that our values for the critical resistance lay quite so exactly on a series of absolutely straight lines. Moreover, we found that the "lower critical voltage" of the lamp was not by any means constant, especially if large parallel capacities were used so that large charges were passed through the lamp at each flash. Under these conditions the extinction voltage for the lamp was considerably higher than that measured when the lamp was running in the steady state, or when a small parallel capacity only was used. Thus the lower critical voltage of a certain lamp was under normal conditions about 140, but when used with a large parallel capacity it rose as high as 220. We would therefore suggest that results based upon the constancy of the lower critical voltage should be accepted with a certain amount of reserve, unless the amounts of charge sent through the lamp at each flash are very small.

XVI.—ON THE THERMO-ELECTRIC PROPERTIES OF BISMUTH ALLOYS,
WITH SPECIAL REFERENCE TO THE EFFECT OF FUSION. WITH A
NOTE ON THERMO-ELECTRIC RE-INVERSION.

By CHARLES ROBERT DARLING, *F.Inst.P., F.I.C.*, and REGINALD HENRY RINALDI.

Received January 11, 1924.

ABSTRACT.

The object of this investigation was to obtain new data regarding the thermo-electric properties of alloys when in the liquid state, and to note specially the nature of the changes, if any, in these properties in the region of the melting point. It was also intended to observe whether thermo-electric effect due to change of state were associated with the alteration in volume at the melting point. A number of different alloys of bismuth with lead and tin respectively were prepared, some of which expanded on freezing, whilst others contracted. The E.M.F. given by these alloys against copper was observed up to 400°C. or over, and it was found that (1) the change in E.M.F. due to the addition of increasing portions of either lead or tin to bismuth reached a maximum value for certain compositions; and (2) that the alloys which expanded appreciably on freezing showed a change in thermo-electric power at the freezing point, whereas with a marked contraction in volume no such change was noted. The methods employed were not sufficiently sensitive to decide whether the point of disappearance of the thermo-electric change was reached in the case of alloys which were unaltered in volume on freezing.

One of the alloys (6.1 per cent Bi, 40 Sn) when coupled with iron, shows the unusual phenomenon of thermo-electric re-inversion. With a cold junction at 0°, this couple shows a zero E.M.F. at 0°, 200°, and again at 350°.

IT is customary for workers on thermo-electricity to cease their observations when the melting point of either member of the couple has been reached, and consequently the thermo-electric properties of fused metals and alloys are almost entirely uncharted. Moreover, the effect of change of state on the thermo-electric power is of much interest, and may, if fully studied, help to an understanding of the real nature of thermo-electricity. In Papers previously read before the Society* it has been shown that whereas the thermo-electric powers of most metals are practically unaffected by fusion, an abrupt change at the melting point is noticed in the cases of bismuth and antimony. It has also been shown by E. F. Northrup† that the resistivities of these two metals are much less in the liquid than in the solid state, whereas the opposite holds true of other metals. Bismuth and antimony are also exceptional in the fact that both expand on solidification, and one of the objects of the present investigation was to attempt to discover whether change in thermo-electric power was always accompanied by increase in volume on freezing, and whether alloys which contract on solidifying behaved as ordinary metals in showing practically no alteration in thermo-electric power on changing state. Such a relation, if established, would be of much interest, as it would raise a question as to why,

* Darling and Grace, Vol. 29, Part 1, and Vol. 30, Part 1.

† Northrup, *Journal Amer. Electrochemical Soc.*, Vol. 25 (1914).

on the breaking down of the crystal structure, the thermo-electric properties of metals are unchanged if the atoms separate to greater distances, but change conspicuously when, on fusion, the atoms approach nearer to each other. A test of the existence of such a relation would appear to be afforded by the examination of a series of alloys of bismuth or antimony with a metal which contracts on freezing, as it is possible to obtain mixtures which either increase, decrease or remain unchanged in volume on solidification, according to the proportions of the constituents. For the present investigation bismuth alloys were chosen, as being easier to work with, and two series were made up, in one of which the added metal was lead and in the other tin. The observations made were intended to note the relation between E.M.F. and temperature, particularly in and beyond the region of the melting point, and also to notice the nature of the volume change on solidification in the case of each alloy.

EXPERIMENTAL.

The method adopted to enable measurements of E.M.F. to be made without interruption by fusion was similar to that described in previous Papers. A crucible *C* (Fig. 1) was fitted into a hole in a sheet of uralite, and filled to overflowing with the alloy under test. A groove leading from the crucible to a silica tube *S*, about

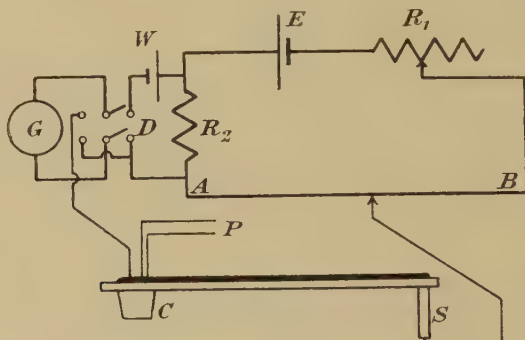


FIG. 1.

60 cm. distant, was also filled with the alloy. The silica tube was filled separately, and a copper wire allowed to freeze into the alloy at one end; the other end was then pushed through a hole in the uralite, and the alloy in the groove joined on to that in the tube by melting. Copper was used as the companion metal of the couples throughout, a wire inserted in the crucible forming the hot junction, whilst the wire in the silica tube constituted the cold junction, which was kept at 0° by surrounding the silica tube with ice. On placing a burner under the crucible the metal in the groove may melt up to a point several centimetres distant from the crucible, but the circuit remains intact.

Readings of E.M.F. were taken by a potentiometer, arranged as in Fig. 1. A stretched wire, *AB*, 1 metre long, was connected in series with a fixed resistance *R*₂, an accumulator *E*, and an adjustable resistance *R*₁. A Weston standard cell *W*, was joined across *R*₂ through a switch *D*, by means of which the galvanometer *G* could be introduced into its circuit. The end *A* of the potentiometer wire, and the

copper wire from the crucible, were connected to the other side of the switch, so that G could be brought into the circuit of the copper-alloy couple. For most of the readings the resistance R_2 was so chosen that on adjusting R_1 so that no deflection occurred on switching the standard cell on to the galvanometer, the fall of pressure along AB was 10 millivolts. As it was found possible to take readings to a limit of accuracy of about 1 mm. on AB , differences of the order of 1/100 of a millivolt could be detected.

Temperatures were measured by means of an iron-constantan thermocouple P , inserted in the crucible, and connected to a millivoltmeter, carefully calibrated to read temperatures. The cold junction of the pyrometer was kept in oil in a vacuum flask, and showed only slight variations during a set of readings.

In order to detect the nature of the change of volume on freezing, an iron mould,

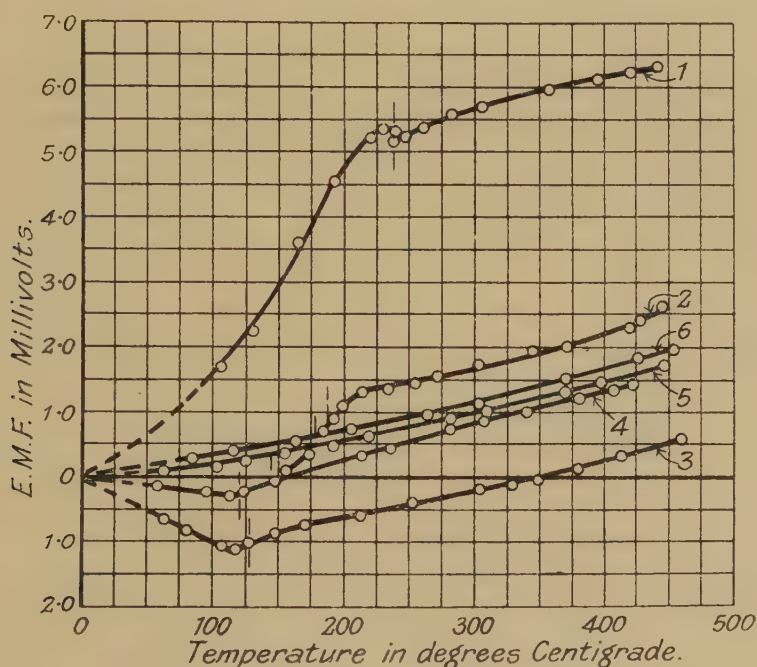


FIG. 2.—BISMUTH-LEAD ALLOYS AGAINST COPPER.

with smooth bottom and sides was used, into which the molten alloy was poured. After solidification a straight-edge was placed on the top surface of the casting, which, if convex, was taken to denote expansion, whilst a hollow surface was assumed to indicate contraction. It is difficult to state to what degree of accuracy change of volume can thus be observed, and our conclusions must be qualified by the limitations of this method, which was adopted in the absence of any other simple test of greater precision.

As is customary in the thermal analysis of alloys, cooling readings were taken at frequent temperature intervals, the corresponding electromotive forces being measured on the potentiometer. Fig. 2 shows graphically the results obtained with the

bismuth-lead alloys, and Fig. 3 the bismuth-tin series. Actual observations are indicated by circles, and freezing points are shown by the short lines touching the curves between the squares. Fig. 4 shows the relation between E.M.F. and tem-

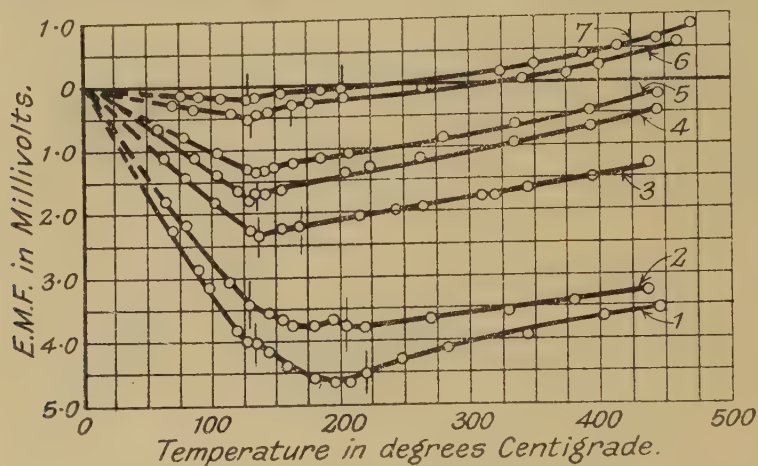


FIG. 3.—BISMUTH-TIN ALLOYS AGAINST COPPER.

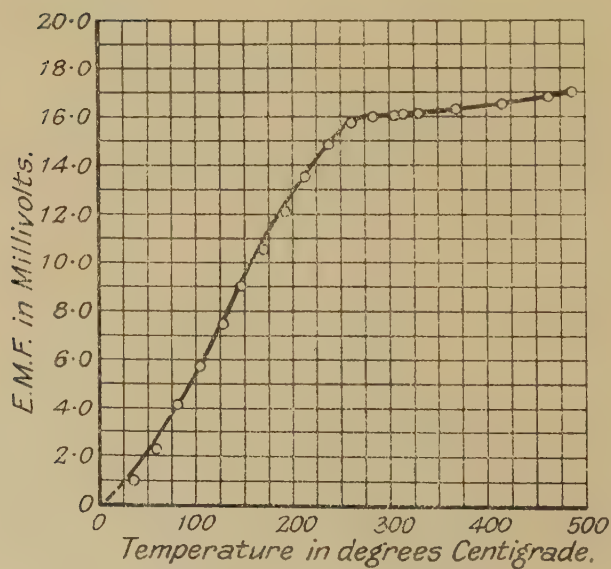


FIG. 4.—BISMUTH AGAINST COPPER.

perature for copper against pure bismuth, and is given for comparison; the curve in this case shows a distinct change of slope at the melting point, 269°C. The com-

position of the alloys corresponding to the numbers opposite the curves are given in tabular form below, together with other special features.

Bismuth-Lead Alloys.

Number.	Percentage of Bismuth.	Freezing Point.	Change of volume on freezing.	Change of Thermo-electric Power on Freezing.
1	90 (by weight)	241°C.	Expanded	Very marked.
2	80	185	Expanded	Marked, but not so abrupt as in 1.
3	70	126	Uncertain	Just noticeable.
4	60	120	Uncertain	Very small, if any.
5	50	144	Contracted	None.
6	40	180	Contracted	None.

All these alloys showed a single, well-marked arrest point, below which solidification was complete. Slight overcooling occurred in the case of No. 1. Comparison with Fig. 4 shows the effect of increasing percentages of lead on the E.M.F., which at 400° is reduced by 60 per cent. on the addition of 10 per cent. of lead. This lowering of E.M.F. is progressive, and when 30 per cent. of lead is present (No. 3), the value has fallen nearly to zero. On the further addition of lead, however, a slight but progressive increase in E.M.F. occurs.

Bismuth-Tin Alloys.

Number.	Percentage of Bismuth.	Arrest Points.	Change of Thermo-electric Power at Arrest Points.
1	90 (by weight)	223°C. and 134°C.	Shown at both.
2	80	210 „ 129	Marked at higher, slight at lower.
3	70	170 „ 136	Shown at lower only.
4	60	135°C.	Noticeable.
5	50	141°C. and 132°C.	Apparent over the temperature region.
6	40	164 „ 131	Slight at higher, present at lower.
7	30	201 „ 130	Absent at higher, present at lower.

This series differs from the lead alloys in the respect that two arrest points are shown, the lower of which corresponds to the freezing of the eutectic, which contains 57 per cent. of bismuth, and the higher to the surplus of either metal over the eutectic composition. Thus in 1, 2 and 3 the upper arrest point is due to the solidification of excess of bismuth, and in 5, 6 and 7 to the surplus of tin. No. 5 is so near the eutectic composition that only one arrest point is detectable with certainty. The alloy corresponding to the eutectic composition, when allowed to freeze in a mould, shows a slightly convex surface, but the actual amount of expansion on solidification is very small. It is doubtful whether our method of judging the change in volume is sufficiently accurate to decide with certainty in the case of this alloy.

The effect of the addition of tin on the E.M.F. is remarkable. Compared with a

junction of copper and pure bismuth, which at 400° gives a positive value of 16.4 millivolts, an alloy containing 10 per cent. of tin gives with copper a negative E.M.F. of 3.6 millivolts, or a total difference of 20 millivolts. Further additions of tin result in a progressive diminution of the negative value, and when more than 60 per cent. of tin is present the E.M.F. at 400° is slightly positive.

INTERPRETATION OF RESULTS.

In the case of the lead alloys, a distinct change in thermo-electric power was shown when a marked increase in volume accompanied solidification. With diminishing expansion this change becomes less marked, and when a notable contraction occurs on freezing no change in thermo-electric power is observable within the limits of accuracy of the experiments. This evidence would appear to support the view that a separation of the atoms to greater distances on freezing causes a change in thermo-electric power, whereas no such change accompanies a closer approach of the atoms. The experimental methods used are not accurate enough to decide whether the change in thermo-electric power vanishes at the point at which the alteration in volume is zero, but with these alloys it becomes less marked as the extent of the expansion on freezing diminishes.

With regard to the tin alloys, it would appear that when the upper arrest point is due to the freezing of excess of bismuth, a change in thermo-electric power occurs, whereas, when tin is present in considerable surplus (No. 7) no such change is observed at the higher freezing point. So far, this is in agreement with the relation between volume change and thermo-electric power previously noted, but no general conclusion can be drawn until observations have been made using larger quantities of alloys, and a more delicate method of measuring E.M.F. It would be of interest to determine whether the thermo-electric effect is the same when a metal freezes out in an alloy, in the presence of other materials, or by itself.

The freezing of the eutectic of bismuth and tin was always accompanied by a change in thermo-electric power, which, however, was never strongly marked. Assuming our observation of the volume change on freezing to be correct, and that a slight expansion occurs, this provides a further case of the association of increase in volume on freezing and change of thermo-electric power.

From another point of view, the results are of interest in showing the effect of the addition of different quantities of a second metal to bismuth, with respect to the E.M.F. developed with a fixed second metal. With both lead and tin a minimum value of E.M.F. at a given temperature is reached, beyond which a progressive increase occurs. Further investigations on these lines would probably yield interesting results, particularly if extended into the region of complete fusion. In the solid state the presence of strain and absence of homogeneity exercise a greater or less influence over the thermo-electric properties, whereas these disturbing factors are absent in the liquid condition, and hence more concordant results may be expected. The data given in the present Paper are a contribution in this direction.

It is hoped to continue the observations with other bismuth alloys, and also with alloys of antimony, with a view to obtaining further evidence regarding the effect of change of volume at fusion on thermo-electric power. Before proceeding to this work, however, we are endeavouring to develop more refined methods of measuring changes in volume and minute differences of E.M.F., so as to enable conclusions to be drawn with a greater degree of certainty.

NOTE ON A CASE OF THERMO-ELECTRIC RE-INVERSION.

If iron is used as companion metal instead of copper with a freshly-prepared alloy composed of 60 per cent. bismuth, and 40 per cent. tin, which melts at 135° , the unusual phenomenon of re-inversion is shown. With the cold junction at 0° , the E.M.F. has a zero value at 0° , 200° (approx.), and 350° (approx.). Between 0° and 200° the E.M.F. is negative, and has a maximum value of about 0.5 millivolt; between 200° and 350° the values are positive, with a maximum of about 0.13 millivolts. Above 350° the E.M.F. is increasingly negative. This phenomenon has been previously noted in the case of steel in the recalescence region,* where, however, it is associated with a molecular transformation. It is of such rare occurrence, however, that this new example was considered worthy of special record.

DISCUSSION.

Dr. J. S. G. THOMAS congratulated the authors on their successful demonstration of the re-inversion described. Benedicks was aware that the effect known by his name would be attributed to strain in the material, and he had carried out experiments in which mercury formed one element of the couple, in order to obviate strain. Had the authors considered the possibility of an electro-thermal effect of this kind located in the molten metal between the hot and cold junctions?

Mr. DARLING replied that judgment must be suspended with regard to the Benedicks effect pending the report of the Committee now sitting upon it. There was a question whether an E.M.F. exists between the molten and solid forms of a metal at the same temperature. American physicists claimed to have detected an E.M.F. of a few microvolts in such circumstances, but this degree of refinement was beyond the capacity of the apparatus described in the Paper.

In reply to a question by Dr. H. BORN, Mr. DARLING said that the experiment on re-inversion could be repeated successfully two or three times in succession, but a kind of fatigue was observable, and, while the E.M.F. curve always showed two turning points, it would not always pass twice through the zero value.

Dr. H. BORN: That is what I expected. The beauty of the authors' experiments is, of course, their great simplicity, but they are very difficult to interpret, and I rather wonder that the curves are not more irregular than they are. When the authors melt alloys in a crucible and allow the liquid to overflow, combination with oxygen and nitrogen will occur and the original homogeneity will be lost. I do not see that such experiments could easily be performed in artificial atmospheres of chemically indifferent gases, but such a course would be advantageous.

Mr. DARLING said that in order to minimise oxidation of the metal this had been coated with carbon; in any case, it was difficult to see how surface oxidation could affect the result.

The PRESIDENT expressed the hope that the authors would settle the questions raised by repeating their experiments in an inert atmosphere with apparatus of sensibility equal to that used by the American workers referred to.

*Belloc, *Ann. de Chim. et de Phys.*, 30, p. 42 (1903).

XVII.—A PRELIMINARY MEASUREMENT OF A PRIMARY GAS-GROWN SKIN.

By J. J. MANLEY, M.A.

(Research Fellow, Magdalen College, Oxford).

Received February 26, 1924.

ABSTRACT.

The Paper deals with an electrical method for detaching a gas-grown skin from a glass surface. Determined in this way, the massiveness of the skin per unit area is shown to be much larger than is generally supposed.

IN this communication is given an account of a preliminary determination of the depth or thickness of the skin that can be formed upon glass by the adsorption of air. Attention is also drawn to the complex nature of the skin.

It is well known that the production and maintenance of high vacua are matters of extreme difficulty even when the vessel that is being evacuated is small and hermetically sealed to the pump. If when a high vacuum has been produced, the pump is for a time kept inactive, the gas pressure within invariably increases and the apparatus has the semblance of being slightly porous. On removing the gas and again leaving the pump at rest, there follows a second growth in the pressure. The experiment may for months be made daily with the result that on every occasion free gas is obtained. If, however, a McLeod gauge be included and the pressure measured as frequently as and just before the pump is used, in the course of some months we find that the daily growth in the pressure very slowly and steadily declines and finally ceases; this gives rise to the conclusion that the gas removed with so much difficulty, was at the outset, present upon the glass in the form of a skin; since, however, this is removable by prolonged pumping, it follows that the skin possesses an appreciable vapour tension. This tension can be balanced and measured by the pressure of the gas emitted by the dwindling skin, as may be shown by the fact that if the pump is kept inactive for a prolonged period and the gas pressure measured daily, a time arrives when no further increase in the pressure is observable.

For measuring the depth of a gas-grown skin, two methods are available: The one is in character adsorptive and the other eruptive. For the adsorptive method, a glass vessel of known dimensions is first simultaneously heated and evacuated to the highest degree possible, and then charged with a known volume of gas, the pressure of which is then periodically determined. When the pressure has become stable, the observed decrease in gaseous volume is a measure of the molecular depth of the skin for the given conditions of temperature and pressure. According to the eruptive method slightly modified and followed in this present instance, a cylindrical glass vessel is filled with the required gas and kept at a known temperature for a considerable time; this allows the glass surface to acquire a maximum skin. Subsequently, the vessel is highly evacuated and thus maintained

until the daily growth in the pressure is inappreciable. The ends of the tube are then covered with long and closely-fitting caps of tin-foil which communicate with the secondary poles of an induction coil. On using the coil a glow discharge fills the tube and at the same time begins to loosen and erupt the gas-grown skin; the resultant free gas is then in a way previously arranged, measured and the depth of the skin calculated.

I now proceed to show that in addition to the skin removable by pumping and by me termed a *secondary* skin, the glass possesses a *primary* and far more permanent one. The evidence for the existence of a primary as distinct from a secondary skin was obtained by experimenting with the chamber of a Töpler pump. First, the whole pump was made chemically clean and dry and charged with highly purified mercury; then for some months the chamber was frequently exhausted until finally the gas pressure was no longer reducible; the pump with its drying tube was then sealed off from all other apparatus and left undisturbed for three years. At the time of sealing the internal pressure as measured by a McLeod gauge, was 4×10^{-5} mm. Immediately before carrying out the concluding part of the experiment, the pump

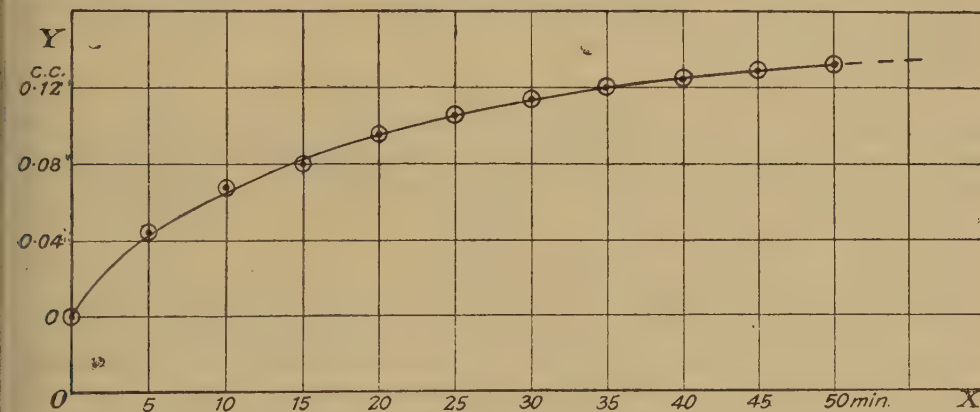


FIG. 1.

was used once in order to remove possible traces of air; a bubble, scarcely discernible, was thus expelled through the fall-tube. The cistern was then lowered and so placed that the chamber of the pump and its side tube were effectively trapped off by mercury from the attached drying tube. Next, the upper half of the chamber was covered with tin-foil and connected by a wire to one pole of an induction coil; a second wire joined the coil to the mercury in the cistern. On closing the primary circuit the chamber was instantly filled with a bright glow yielding a many-line spectrum. After 5 minutes the current was stopped, and the cistern slowly raised to transfer free gas from the chamber to the upper portion of the fall-tube; there it was retained until its pressure and columnar length had been measured; the bore of the fall-tube was known and therefore the volume of the gas was now calculable. Finally, the gas was ejected and the cistern replaced. These operations were performed ten times. During these ten five-minute periods, the total volume of gas produced was 0.1324 cubic cm., the pressure being normal and the temperature 15°C . The largest individual volume 0.0445 cubic cm. was obtained during the

first and the smallest 0.0033 cubic cm., during the last period. The results are graphed in the accompanying Fig. 1, wherein the volumes are plotted along *OY* and the periods along *OX*. Apart from three balancing irregularities probably resulting from variations in the applied high E.M.F., the curve is surprisingly smooth, and of the determined points, seven lie upon the graph, the terminal slope of which approximately corresponds to a mean rate of eruption of 0.0009 cubic cm. of gas per minute. As this was still the rate when the experiment was concluded, the complete removal of a gas-grown skin is very possibly a lengthy matter. The area from which the gas was erupted being known, it was easy to calculate the number of superposed molecules liberated during the whole period of 50 minutes. For this purpose the following data were used :—

Internal area of glass chamber = 230 sq. cm.

Diameter of air molecule = 3.72×10^{-8} cm. (J. H. Jeans).

Number of molecules = 6×10^{23} per 22,400 cubic cm.

Volume of erupted skin measured as air = 0.123 cubic cm. at N.T.P.

From the above it is found that the erupted skin which on account of its persistence for three years may be regarded as a normal one, had a minimum depth of 20 molecules ; a value which is much higher than that usually given by Langmuir and others.

The experiment just described is of a preliminary kind only ; consequently its form is imperfect. The chief objection arises from the probability that some of the erupted skin measured as gas, was derived from the mercury in the chamber. A similar objection to the presence of mercury likewise holds for experiments conducted by the adsorptive method. An extension of this present investigation has been planned ; and in the new apparatus mercury will be excluded during the eruption of the skin. In due time therefore I hope to give more precise information concerning the molecular depth of a skin as determined by the eruptive method.

In conclusion, it may be pointed out that from my experiments it appears (1) that a nude surface when brought into contact with a gas, first acquires a true, permanent and primary skin which under all ordinary conditions is retained even in the presence of high vacua ; and (2) that the completed primary skin adsorbs a quantity of its parent gas in much the same way as solids in general do. According to this view the skin which I have termed secondary is not a true skin, but a certain mass of gas which varies with temperature, pressure, &c., condensed upon and commingled with the molecular groups forming the true and primary skin.

DISCUSSION.

For Discussion see page 293.

XVIII.—ON THE REMOVAL OF GAS-GROWN SKINS FROM A SPRENGEL PUMP.

By J. J. MANLEY, *M.A.*

(Research Fellow, Magdalen College, Oxford).

Received March 11, 1924.

ABSTRACT.

The pump possesses two vacuum tubes which are interposed between the cistern and the fall-tube. The vacuum tubes have external electrodes. When the pump is in use the electrodes are activated; and the mercury, in falling through the glow discharges, is largely freed from condensed and adsorbed gases.

IN a former communication* it was shown that by giving the Sprengel pump an appropriate form and by adopting a certain procedure, the gas-grown skins upon the interior surfaces can be removed and their re-formation prevented for a very considerable time. It must, however, be admitted that the form of the pump is somewhat complicated and therefore correspondingly costly; also, that the preliminary operations involved in preparing it for use are intricate and not easily repeatable; but as the absence of gas-grown skins secures for the worker such marked advantages as (1) a greater efficiency on the part of the pump, and (2) freedom from impurities resulting from erosion of the skin by the flowing mercury, such objections would in some cases have but little weight. During the past year, however, attempts have been made (*a*) to simplify the structure of the pump and (*b*) to discover some more convenient method for removing the skin: these objects have now been attained by the construction of a pump having the form shown in Fig. 1. The success of the new pump is based upon the fact that if a highly-exhausted tube is fitted with external electrodes activated by a powerful induction coil, the glow discharges transform the skins of the inner surfaces, into free gases. The present pump therefore differs from the usual type, chiefly in respect of two vacuum chambers A, B, having external electrodes C, D. These electrodes are made of tin-foil strips 7 cm. wide and 30 cm. long; they are attached in the following way:—

First the inside of a strip is evenly coated with concentrated shellac varnish and one end placed upon the glass, so that it is parallel to the axis of the tube; then the foil is continuously wound and at the same time gently rubbed to expel air bubbles. When the winding is complete the newly formed electrode is varnished and given a connector for the induction coil. The connector consists of a duplicated band of tin-foil, in one end of which is embedded a wire having a protruding loop.

The band is wound upon the electrode after the manner described above, and its position is secured by two turns of adhesive tape. Built thus, the electrodes are extremely reliable, and, provided the applied E.M.F. is not excessive, the supporting glass tubes are but rarely pierced by a discharge.

For removing aqueous vapour, use is made of two communicating drying bulbs E, F; these are charged with phosphorus pentoxide rendered pure by ozonised air.†

The several parts of the apparatus are chemically cleaned and dried just before they are joined together to form the complete pump. The pump, having been

* *Proc. Phys. Soc.*, Vol. 34, Part 3, p. 86.

† *Trans. Chem. Soc.*, Vol. 121, p. 331 (1922).

set up and joined by means of the tube T, to a Töpler or other auxiliary pump, is prepared for use as follows :—

First, the tap G is closed ; then the cisterns P and S are charged with highly purified mercury ; next the head Q is connected through a drying-tube with a Geryk

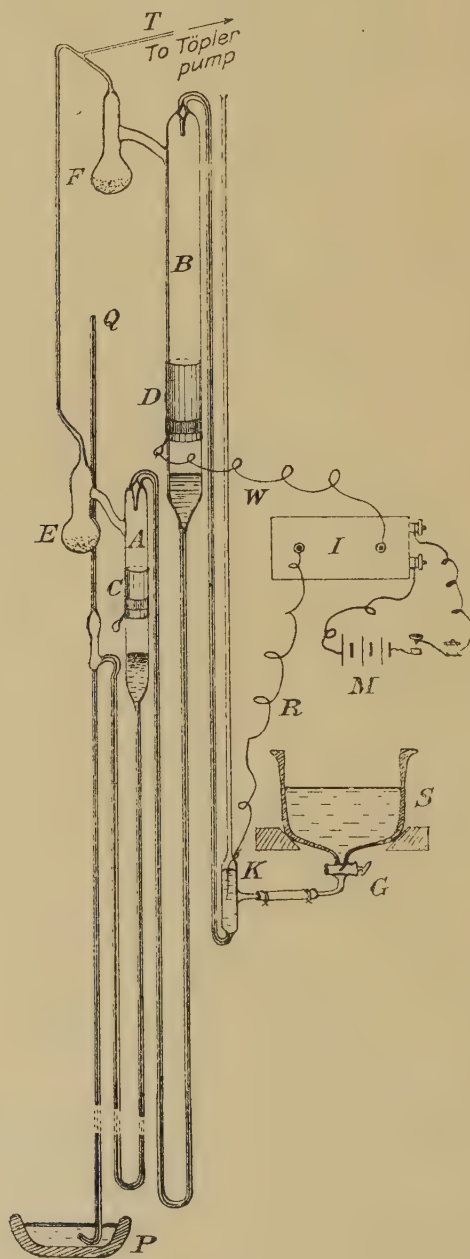


FIG. 1.

or other manual pump, and the ends of all open tubes having been closed by air-tight caps, the Sprengel pump is then highly exhausted and the whole carefully heated. Next, the apparatus is re-filled by slowly admitting air through the drying-tube; then again exhausted and re-heated. These several operations having been performed a few times, and the pump highly exhausted, the cap is removed from the submerged end of the fall-tube and the tap G opened so as to charge the tubes with mercury; the pump is now ready for use and the vessel to be evacuated may be fused to Q. A very decided advantage is, however, gained if, instead of joining the vessel to Q direct, a barometric trap* is interposed between the two.

In evacuating any vessel most of the air is first removed by a Geryk pump which is then trapped off by mercury in the usual way. The Sprengel pump is now brought into use, and when the vacuum is high the secondary poles of an induction coil I are connected, the one with the electrode D, and the other with the platinum wire sealed into the reservoir K. On using the coil, which is worked by a battery M of 3 accumulators in series, the whole of the chamber B is filled with an ordinary glow discharge; this gradually transforms the gas-grown skin found upon the interior surfaces, into free gases; also, the drops of mercury as they fall from the jet, are shattered and at the same time largely robbed of occluded and condensed gases; these gases are at frequent intervals, withdrawn from B by the pump operating through T. After a time the other chamber A is similarly treated; and for this purpose the wire R is transferred from K to C. It may be noted that when the poles of the coil are joined, the one to C and the other to K, both chambers may be simultaneously subjected to the influence of the glow. Proceeding thus, and alternately exciting A and B, but chiefly B, the efficiency of the pump rapidly increases and after a time bubbles fail to appear in the bend leading into the fall-tube. From this time onward any change in the working of the pump is in the direction of a maximum efficiency; and, provided the head is always trapped off by a barometric column, prior to the opening or removal of an evacuated vessel, it follows theoretically that the more largely the pump is used the greater does its efficiency become.

DISCUSSION on Papers XVII. and XVIII.

Dr. J. S. G. THOMAS said that all admired the patience which the author had devoted to the improvement of the mercury pump. Would it be possible to get rid of the primary skin with the modern condensation or jet pump?

The AUTHOR said that he had not tried the jet pump, as his ultimate object was to perfect a circulator for helium and its congeners, for which purpose a Sprengel pump was more convenient than a jet pump. He thought the latter could probably be used as suggested.

Mr. F. E. SMITH inquired whether the investigations described had been extended to skins on the walls of silica vessels. The latter were of practical importance in view of the increasing use of silica for thermionic valves.

The AUTHOR replied that he had not investigated silica, but he had little doubt that the results would be similar to those described. He would recommend the use of external electrodes for clearing silica vessels. His experiments had proved that glass is not porous, as was once suspected.

Dr. D. OWEN asked whether the "primary" skin was to be regarded as in the solid or liquid state. What assumption had been made as to the distance apart and arrangement of the molecules in calculating the depth of the skin?

The AUTHOR replied that the skin appeared to be in a state between that of a liquid and a solid. He had calculated the *minimum* depth by assuming that the molecules were in contact and had gas-kinetic diameters. Langmuir in his experiments on the addition of two layers of molecules at a surface had assumed that these made up the whole thickness of the skin; his own conclusion was that there were really at least 20 such layers. He hoped to make similar measurements on other gases, particularly the inert gases.

* Proc. Phys. Soc., Vol. 35, Part 3, p. 137.

XIX.—THE “ DIAMETRAL PLANE ” IN ELEMENTARY OPTICS.

By CHARLES H. LEES, *D.Sc., F.R.S.*

ABSTRACT.

It is shown that a simple graphical method suitable for use in elementary optics may be based on the relation between the distances from the centre of curvature of the points at which the rays at a refracting spherical surface cross the diametral plane of the surface.

I. INTRODUCTION.

IT is usual in elementary optics to specify a thin lens by its focal length in vacuum or in air, which to the degree of accuracy contemplated has an index of refraction = 1. When the lens has to be used in a medium of index other than 1 its focal length in the new medium cannot be found from its vacuum value without a knowledge of the refractive index of the material of the lens itself. If further the lens separates two media of different refractive indices its two focal lengths cannot be found without a knowledge of its refractive index, its two radii of curvature and the refractive indices of the two media. While for many purposes the specification of the vacuum or air focal length of a thin lens is sufficient, the specification is incomplete unless its two radii of curvature and the refractive index of, or the speed of light in, its material are given. Thus, 24, 1·52, —4 or 24, 1·98, —4 the 10^{10} being omitted, would define a “ crossed lens ” completely, and would enable its behaviour under any conditions to be determined. In cases in which the vacuum focal length alone were required it could be calculated from the data given, and used in any formula involving focal lengths. For the more general cases involving media other than air the above specification gives just those quantities required in the formulæ established for thin lenses. For thick lenses the distance apart of the two surfaces must also be given so that the specification is of the form 24, (1·52, ·8), —4 or 24, (1·98, ·8), —4.

When we pass from the analytical expressions to the graphical methods generally used we find that the latter almost all depend on a knowledge of the positions of the two foci, and any specification which does not give the focal length or focal lengths appears at first sight to involve a calculation of one or both quantities before graphical methods can be utilised. This is, however, not the case, and it is the object of the following pages to show that a graphical method applicable over a wide field flows naturally out of the specification of a lens by its radii of curvature, its refractive index, and the distance of its surfaces apart.

II. REFRACTION AT A SPHERICAL SURFACE.

The fundamental problem of elementary geometrical optics—the refraction at a single spherical surface—receives little attention in elementary text books, as compared with that devoted to mirrors and lenses, owing probably to the fact that it introduces at once the difficulties of the two focal lengths and the proper directions in which they should be measured from the surface in the different cases which may

arise, while for mirrors and for lenses in single media only one focal length is involved. In what follows refraction of paraxial rays at a single spherical surface to the order of approximation usual in elementary theory is regarded as the starting point. The surface at which refraction takes place will be replaced by the tangent plane at its vertex—the “vertex plane”—and the parallel plane through the centre of curvature of the surface will be called the “diametral plane.”

The elementary theory of refraction at a spherical surface may be reproduced as follows:—

Let AC , Fig. 1, be the axis of a beam proceeding to Q_1 , PQ_1 one of the rays and A the vertex of a spherical surface AP , separating media 1 and 2, in which the velocities of light are v_1 and v_2 respectively, and let C be the centre of curva-

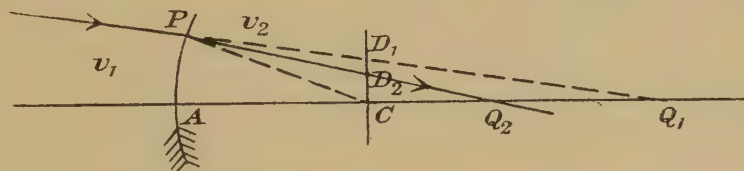


FIG. 1.

$$\left(PQ_1 \text{ incident, } PQ_2 \text{ refracted ray, } \frac{CD_1}{v_1} = \frac{CD_2}{v_2} \right).$$

ture of the surface. Let the ray PQ_1 in the first medium give rise to the ray PQ_2 in the second.

Then, if i_1 and i_2 are the angles of incidence and refraction at P the law of refraction gives us

$$\frac{\sin i_1}{v_1} = \frac{\sin i_2}{v_2} \quad \dots \dots \dots (2.1)$$

If i_1 and i_2 are small this becomes $i_1/v_1 = i_2/v_2$.

If the angles of inclination of PC , PQ_1 and PQ_2 to the axis AQ be written \hat{C} , \hat{Q}_1 , \hat{Q}_2 respectively, we have $i_1 = \hat{C} - \hat{Q}_1$, $i_2 = \hat{C} - \hat{Q}_2$, and the equation becomes

$$\frac{\hat{C} - \hat{Q}_1}{v_1} = \frac{\hat{C} - \hat{Q}_2}{v_2},$$

which gives

$$\frac{AP}{v_1} \left(\frac{1}{AC} - \frac{1}{AQ_1} \right) = \frac{AP}{v_2} \left(\frac{1}{AC} - \frac{1}{AQ_2} \right),$$

or writing

$$AC = r, AQ_1 = u_1, AQ_2 = u_2 \quad \frac{AP}{v_1} \left(\frac{1}{r} - \frac{1}{u_1} \right) = \frac{AP}{v_2} \left(\frac{1}{r} - \frac{1}{u_2} \right), \quad \dots \dots (2.2)$$

and

$$\frac{1}{v_1} \left(\frac{1}{r} - \frac{1}{u_1} \right) = \frac{1}{v_2} \left(\frac{1}{r} - \frac{1}{u_2} \right), \quad \dots \dots \dots (2.3)$$

the usual equation.

Since the angles of inclination of the radius and rays to the axis are small the arc AP may be taken as coincident with its tangent at A , that is, the surface of separation of the media may be taken as identical with the vertex plane.

III. THE GRAPHICAL METHOD.

Through C draw the diametral plane parallel to the vertex plane, cutting the rays PQ_1, PQ_2 in D_1 and D_2 respectively. Then, since (2.2) gives

$$\frac{AP}{v_1} \cdot \frac{u_1 - r}{u_1} = \frac{AP}{v_2} \cdot \frac{u_2 - r}{u_2},$$

we get by similar triangles

$$CD_1/v_1 = CD_2/v_2, \quad \dots \dots \dots (3.1)$$

the relation which gives the diametral plane its value. It holds only to the degree of approximation for which (2.3) is true.* It leads to the following simple construction for the refracted ray:—

Let AC be the axis of a beam proceeding to Q_1 , AP , Fig. 2, be the vertex plane of the spherical surface separating media in which the light travels with speeds v_1 and v_2 respectively, CD_1 the parallel diametral plane through C the centre of curvature, and let PQ_1 be a ray in the first medium, cutting the vertex plane in P , and the diametral plane in D_1 . Take CD_2 along CD_1 , such that $CD_2/CD_1 = v_2/v_1$, join D_2 to P , and produce to cut AQ_1 in Q_2 . Then PD_2Q_2 is the refracted ray.†

The intersection of the ray with the diametral plane is real for the ray in the

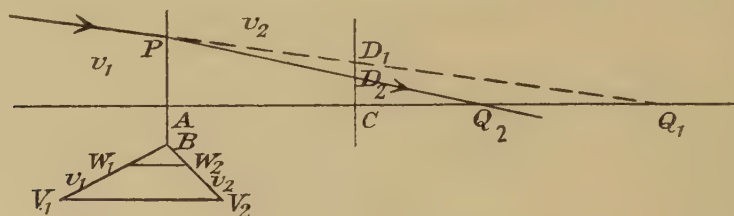


FIG. 2.

$$\left(PQ_1 \text{ incident, } PQ_2 \text{ refracted ray, } BW_1 = CD_1, BW_2 = CD_2, \frac{CD_1}{v_1} = \frac{CD_2}{v_2} \right).$$

medium on the concave side of the surface and unreal for the ray in the medium on the convex side. Unreal rays are indicated by dotted lines in the figures.

A graphical method of cutting off lengths in the diametral plane proportional to the velocities in the media on the two sides of the spherical surface may be used, but it has been found more convenient to carry out the construction at the vertex plane.

From a point B in the vertex plane, Fig. 2, two lengths, BV_1, BV_2 , proportional respectively to the velocities v_1, v_2 of light in the two media on the two sides of the plane, are measured in sloping directions downwards into their respective media so that each ends in the same straight line parallel to the axis of the refracting surface. Any straight line parallel to the axis cuts off lengths from the sloping lines proportional to the velocities of light in the two media, and these lengths are transferred to the diametral plane.

* If any plane be drawn parallel to the vertex and diametral planes, and PC, PD_1, PD_2 cut it in Y_0, Y_1, Y_2 , we have to the same degree of approximation $\frac{Y_0 Y_1}{v_1} = \frac{Y_0 Y_2}{v_2}$.

† The construction is the same whether C lies between A and Q or outside them.

IV. LENGTHS OF OBJECT AND IMAGE.

The construction of Fig. 2 leads directly without the introduction of further approximations to the usual expressions for the relative lengths of object and image when they are short lines either along or perpendicular to the axis.

A. When Along the Axis.

Writing $AP=b$, $CD_1=v_1c$, $CD_2=v_2c$, we have

$$u_1=r\frac{b}{b-v_1c}, u_2=r\frac{b}{b-v_2c} \quad \dots \quad (4.1)^*$$

If, then c increases by the small amount c' , and this causes an increase u'_1 in u_1 and u'_2 in u_2 we have

$$\left. \begin{aligned} u'_1 &= \frac{r}{b} \left(\frac{b}{b-v_1c} \right)^2 v_1 c' = \frac{r}{b} \left(\frac{u_1}{r} \right)^2 v_1 c' \\ u'_2 &= \frac{r}{b} \left(\frac{b}{b-v_2c} \right)^2 v_2 c' = \frac{r}{b} \left(\frac{u_2}{r} \right)^2 v_2 c' \end{aligned} \right\} \quad \dots \quad (4.2)$$

and

$$\frac{u'_1}{u_2} = \left(\frac{u_1}{u_2} \right)^2 \left(\frac{v_1}{v_2} \right) \quad \dots \quad (4.3)$$

Hence,

or lengths of object and image are proportional to the squares of their distances from the vertex plane, and to the velocities in their respective media.

B. When Perpendicular to the Axis.

If a short straight line of length a_1 is erected perpendicular to the axis at Q_1 and the top of it is joined to P , the intercept on the diametral plane becomes $v_1(c+c')$ where c' is small. The image of a_1 is a straight line of length a_2 perpendicular to the axis at Q_2 and when the top of it is joined to P the intercept on the diametral plane becomes $v_2(c+c')$.

Hence

$$a_1 = \frac{u_1}{r} v_1 c' \quad \text{and} \quad a_2 = \frac{u_2}{r} v_2 c' \quad \dots \quad (4.5)$$

Thus

$$\frac{a_1}{a_2} = \frac{u_1}{u_2} \cdot \frac{v_1}{v_2} \quad \dots \quad (4.6)$$

or lengths of object and image perpendicular to the axis are proportional to their distances from the vertex plane, and to the velocities in their respective media.

In the special cases in which r is large compared to u_1 and u_2 Fig. 2 gives

$$u_1 = \pm \frac{rb}{v_1c}, \quad u_2 = \pm \frac{rb}{v_2c} \quad \text{or} \quad u_1 v_1 = u_2 v_2$$

very nearly, and equation (4.3) becomes $\frac{u'_1}{u'_2} = \frac{u_1}{u_2} = \frac{v_2}{v_1}$ very nearly, or the lengths of object and image when along the axis and near the surface are nearly proportional to their distances from the surface or to the reciprocals of the speeds in their respective media. For lengths perpendicular to the axis the relation (4.6) gives $a_1=a_2$ or object and image are equal.

* The denominators are $b+v_1c$ and $b+v_2c$, if P and D_1D_2 are on opposite sides of the axis.

velocity of light in the medium in which the ray is travelling. It is convenient to draw the velocity lines for the second vertex below or above those for the first as in Fig. 4.

The method of determining the emergent ray is the same in all cases, whether the lens is thick or thin, whether the media on the two sides of it are identical or not, and whether the speed of light is less or greater in the lens than in the media on the two sides of it.

VIII. THIN LENSES IN A SINGLE MEDIUM.

The case most often treated in elementary works is that of a thin lens in a single medium. The two vertex planes then coincide at A , but the determination of the emergent ray is unaffected, except that the ratios of the intercepts of the rays on the diametral planes are now identical. If A , C_{12} and C_{21} the vertex, centre of curvature of the first and that of the second respectively are written down in the order in which the light passes through them, and the subscripts of the C 's, 1 referring to the surrounding medium and 2 to that of the lens, are written in the same order, the lens

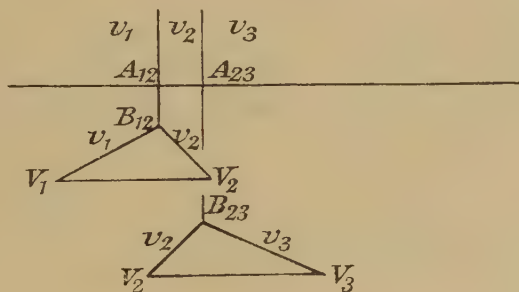


FIG. 4.

(Vertex planes for a thick lens separating different media).

is converging if the C subscript next to A is that of the medium in which the speed of light is the larger, and is diverging if the subscript is that in which the speed is smaller.

IX. CONCLUSION.

The previous paragraphs are sufficient to show that a considerable simplification and unification of the graphical methods of treating elementary optics may be secured by the use of the diametral planes and their properties.

DISCUSSION.

Mr. T. SMITH said he had some hesitation in speaking on this Paper, for the subject appeared very differently to the teacher and to the optician. Indeed, it seemed that in optics one could be either intelligible or accurate, but not both. His observations were made from a point of view which the author might well claim to be without importance for the teacher.

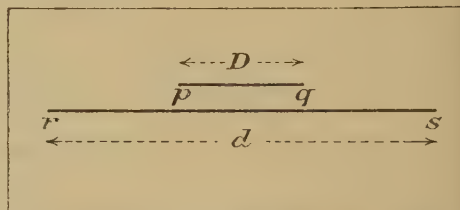
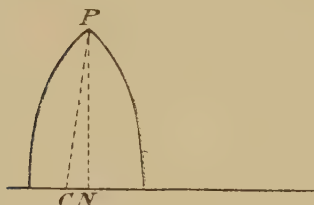
From the practical point of view, a thin lens is specified by one quantity—its power—which represents the instantaneous change of curvature suffered by a wave front in passing through a lens. All problems are capable of treatment in terms of the lens as the element if the thick plate is included as a special case. For instance, in immersion microscopy, the immersion fluid is taken as a parallel liquid plate, and the specimen under examination may be regarded as separated

from the mounting medium by an indefinitely thin film of air. This combination of a plate with a lens should remove the student's difficulty in dealing with cases in which the external media are different. The real objection to this treatment—that some rays would be reflected instead of refracted were an air film actually present—is not likely to occur to the student. This point does not arise where small angles of incidence are involved.

In specifying a lens the rational procedure consists in giving curvatures rather than radii, since a high percentage accuracy is important in short radii, and a very rough approximation, such as the first figure only, in long radii.

Prof. Lees' treatment of the geometrical method was no doubt based on an intimate knowledge of the student. One would, however, expect the student to observe that in a sphere every plane through the centre is a diametral plane, but that different planes in this construction give different results. It should therefore be pointed out that the relation used applies strictly to the perpendiculars to the rays. The construction of the Paper would be exactly true for collinear imagery, and the distinction between these intercepts and the perpendiculars illustrates that collinear imagery is not attainable. Young's construction for refraction at a spherical surface, which is as simple as the author's and is exact, is worth consideration as a basis of an elementary geometrical treatment, and has the special advantage of drawing attention to the aplanatic spheres which are of such importance in the construction of certain lens systems.

Mr. THOMAS H. BLAKESLEY admitted that he had been allured to the meeting of the Society by the title which had been given by the author to his Paper, inasmuch as he himself had been, in days gone by, somewhat of a revolutionary in the matter of geometrical optics. Everyone knows that the geometrical shape of the lens is determined by two radii of face curvature and a length along the axis separating the faces, and that the various optical characters require something more, usually the index of refraction for the light employed, for complete determination. But it by no means follows that the quantities treated as fundamental are the best for



formulation of properties. The author clearly thinks otherwise, and in this he has the speaker's sympathy and best wishes for success.

Suppose as a case, among many other possibilities, that in the section of the lens containing the axis the two faces meet in an angle equal to 2β at the point P. From P draw PC bisecting this horn-angle, and PN at right angles to the axis, and call the angle NPC α and call PN h .

Then the focal length generally is equal to

$$-\frac{h \cos \beta}{\sin 2\beta} \cdot \frac{\mu}{\mu-1} \cdot \frac{1}{\cos \alpha + \frac{\mu-1}{\mu} \cos \beta}$$

and taking the usual steps to find when this can be a maximum or minimum, the condition appears that $\cos \alpha = \mu^2 - 1 \cdot -\cos \beta$, and under these circumstances the focal length is

$$\frac{h}{\mu-1^2 \cdot \sin 2\beta}$$

When the more ordinary quantities, viz.,

r_1 , the radius of the first surface encountered by the light ;

r_2 , the radius of the second surface encountered by the light ;

d , the thickness of the lens at the axis ;

μ , the index of refraction ;

are employed as fundamental, all the four being mutually independent, and sufficient for generality, the treatment will be much the same.

It may be mentioned that the symbols above given for the face radii, viz., r_1 and r_2 , are considered to have positive values when the light in its passage passes the centres of curvature *before* encountering the corresponding surfaces. This corresponds with the usual treatment of curved mirrors.

With these conventions the value for the reciprocal $\frac{1}{f}$ of the focal length f is expressed by

$$\frac{1}{f} = \frac{1}{r_1 r_2} \cdot \frac{\mu - 1}{\mu} \left\{ -d - \mu(d - r_2 + r_1) \right\}$$

from which the differential coefficient with regard to μ is—

$$\frac{df}{d\mu} = -\frac{1}{r_1 r_2} \left\{ \frac{d}{\mu^2} - (d - r_2 + r_1) \right\}$$

which is zero when $d = \mu^2(d - r_2 + r_1)$, an expression being still more simple when it is pointed out that $(d - r_2 + r_1)$ is merely the distance from the first centre of curvature to the second, measured positively down the stream of light, and calling this D

$$d = \mu^2 D$$

If two straight lines pq , rs , of which $pq = \mu^2 rs$, capable of sliding one upon the other, are in any position as shown, and spheres are struck from centres p and q , at distances pr , qs , through r and s , and the space indicated filled with a medium whose index is μ , it will constitute a lens achromatic in the sense often employed of having focal lengths running in pairs which are equal, and coalescing in a maximum or minimum value (according to convention in signs) at the index considered. And, further, if μ_1 be a little in excess of μ , the focal length will be equal to that for μ_2 , a little in defect of μ , if $\mu_1 \mu_2 = \mu^2$.

If equality of focal length in respect of two indices is required, we may calculate the relation of rs to pq as $rs = \mu_1 \mu_2 pq$. We shall so obtain the required equality in focal lengths, and if curiosity should require the particular index for the maximum effect it may be obtained from $\mu = \sqrt{\mu_1 \mu_2}$.

Mr. T. SMITH (subsequently communicated): The difficulty mentioned by Prof. Lees in his reply as to the axis along which the foci should be measured in the case of a spherical surface is surmounted by pointing out that, strictly, focal lengths are measurable along the actual ray, not along the axis.

Mr. ROLLO APPLEYARD (communicated): In a Paper read before the Physical Society on June 11, 1897, and published in the *Philosophical Magazine* of August, 1897, Prof. T. H. Blakesley examined the question of definition of "focal length," and urged physicists to revise their ideas concerning the matter. It is to be desired that the present contribution to the subject by Prof. C. H. Lees should be considered in association with that of Prof. Blakesley, and that the opportunity should be taken to examine whether it is possible to free our definitions from difficulties such as arise from having to take into account the thickness of the lens. The arguments of Prof. Blakesley deserve closer attention than they have received. Briefly, he points out that "focal length" should be defined as an abstract length—a straight-line characteristic of the lens or lens-combination. It is thus analogous to the inductance of a helix, and we do not confuse the length of the helix with the abstract length denoting the inductance. He then explains that any function of the respective distances of object and image from their appropriate focal centres, and the focal length, may be employed in conjunction with the usual v , u , f formula to eliminate either of those distances. He selects the magnification m as such a function, and writing v for the distance from any fixed point on the axis, measured positively in the direction of the light, to the position of one of a pair of conjugate foci on that axis of a coaxial lens-system, he obtains

$$\frac{dv}{dm} = f = \text{focal length} = \text{constant.}$$

And similarly for the other focus, which may be in a second medium,

$$\frac{du}{d(1/m)} = f_1$$

or

$$\frac{v-v_0}{u-u_0} = \frac{f}{f_1} m^2$$

from which he derives a complete system for expressing in a simple manner the required characteristic lengths for any lens or mirror. The question is dealt with in greater detail in his "Geometrical Optics," published in 1903, and long since out of print. It is noteworthy that the function selected by Prof. Lees is not the magnification, but the relation of the distances from the centre of curvature of the points at which the rays cross the "diametral" plane in the case he has chosen. Consequently his valuable paper may be regarded as a further illustration of the principle that focal length is primarily an abstract characteristic, to be determined in various ways according to what function is selected for the elimination process—but preferably, perhaps, by the selection of magnification.

The AUTHOR, in reply to the discussion, said that he had tried the use of curvature in teaching elementary optics, but students at the stage of knowledge he had in mind did not, in practice, readily respond to this method, and he had had to abandon it. A student who is supposed to know enough to calculate the image in air of a lamp in a glass tank with a lens in its side very frequently makes mistakes in dealing with focal lengths, whereas radii of curvature make a more direct appeal to him. The fact that the axis is to some extent arbitrary in the method described is a weakness, but one that is shared with the usual methods depending on focal length.

XX.—APPARATUS FOR THE DETERMINATION OF THE HEAT OF
EVAPORATION OF LIQUIDS OF HIGH BOILING POINTS.

By J. H. AWBERY, *B.A., B.Sc.*, and EZER GRIFFITHS, *D.Sc.*, The National Physical
Laboratory.

Received March 18, 1924.

ABSTRACT.

Two new forms of apparatus for determining the heat of evaporation of liquids of high boiling point are described, and their relative merits briefly discussed.

In the one the determination is made by a measurement of the amount of liquid vapourised for a given energy supply (radiation loss being eliminated by means of a constant temperature jacket) and in the other, the energy given up on condensing is estimated by means of a continuous flow calorimeter. The latter is thus a modification of the well-known apparatus of Berthelot, but particular attention has been paid to the avoidance of defects inherent in earlier types of apparatus.

The apparatus have been tested by determining with them the heats of evaporation of such liquids as alcohol, water, and aniline, whose heats of evaporation are well known.

A brief survey of the earlier work is included, and a number of references given.

INTRODUCTION.

DURING the course of some general investigations, it became necessary to determine the heats of evaporation of some liquids boiling at temperatures from 300 to 400°C.

The high temperatures involved rendered the utilisation of the customary forms of apparatus extremely difficult, so modifications had to be made to meet the special requirements of the case.

The apparatus hitherto employed for latent heat measurements may be broadly classified under two heads: In the one the quantity of heat liberated on the condensation of a definite weight of vapour is measured. In the other the heat which must be supplied to the liquid to produce a certain weight of vapour is measured.

All the earlier forms of apparatus belong to the first class for the simple reason that gas heating was almost universal at the time of their origin, and it is only the development of electrical measurements that has rendered possible the use of the second method.

In this Paper it is not necessary to dwell in detail on the historical apparatus, but in passing one must pay tribute to the insight shown by Regnault* in designing his apparatus on a really large scale, and thereby minimising the errors inherent in the first method. We employed this method, and made two modifications which are obvious in the present state of our knowledge of calorimetry, namely, the application of the continuous flow calorimeter and of electrical heating.

This rendered possible the carrying out of an experiment under steady conditions, and, furthermore, the length of the connecting tube between boiler and calorimeter was cut down to a minimum, thereby avoiding premature condensation.

* *Mem. de l'Inst. de France*, 21, 638 (1847).

The second method of measurement, in which heat input is the quantity observed, appealed to us on account of the ease with which heat can be measured in the form of electrical energy, and a type of apparatus was devised working on this principle. Existing forms of apparatus did not afford us much help in the design, since they had been developed with a view to tests on liquids of low boiling points.

It may be of interest before passing on to a description of our own apparatus to indicate the development made by previous investigators.

Following on Regnault, Berthelot* is the most noteworthy worker in this field. He produced a laboratory form of apparatus where the liquid was boiled in a bulb and the vapour carried into the calorimeter through a tube projecting up through the centre.

When a ring burner is employed for heating, there is a tendency for superheating of the vapour to take place in this form of apparatus. This apparatus was improved in details by Schiff† and Louguine.‡

Harker§ substituted internal electrical heating for the gas ring and also devised an ingenious form of valve. He emphasised the difficulty due to condensation of the vapour in the tubes and the carrying over of minute liquid particles.

Dr. E. H. Griffiths|| brought the electrical method to a high degree of perfection for determination at temperatures below 100°C. He also made an absolute determination of the latent heat of benzene to serve as standard for Sir William Ramsay and Miss Marshall¶ in their comparative apparatus for latent heat determinations. Their apparatus consisted essentially of a glass globe similar to a lamp bulb which was enclosed in a jacket of the vapour of the same liquid as that under test. It was assumed that by this arrangement heat loss or gain by the liquid within the bulb was completely prevented. The electrical energy was not directly measured, but a similar apparatus with benzene was used as a standard, the two heating resistances being in series.

It seems to us that the apparatus could be improved by the use of a double-walled enclosure for the bulb, so as to offer greater thermal resistance to the heat flow should the temperatures within and without the globe not be identical.

In our apparatus this principle was adopted and, furthermore, the heat input was measured as electrical energy, since electrical measurements present nothing like the same difficulties to-day as they did 30 years ago, when Ramsay and Marshall carried out their experiments.

In addition to the above-mentioned Papers, reference might be made to the following :—

Trautz (*Zs. Elch.*, 14, 271, 1908) ; Henning (*Ann. d. Phys.*, 29, 441, 1909) ; A. C. Smith (*Edinburgh Proc.*, 24, 450, 1903) ; A. W. Smith (*Phys. Rev.*, 33, 173, 1911) ; Nagornow and Rotinjanz (*Zs. Ph. Ch.*, 77, 700, 1911) ; and Kahlenberg (*J. Phys. Chem.*, 5, 215, 1901). *See also* Glazebrook's *Dictionary of Applied Physics*, Vol. I., p. 550.

We turn now to our own apparatus.

* *Comptes Rendus*, 85, 646.

† *Liebig's Annalen*, 234, 338 (1886).

‡ *Ann. Chim. Phys.*, 7, 251 (1896), and 13, 337 (1898).

§ *Memo. Manchester Lit. & Phil. Soc.* (4), 10, 38 (1896).

|| *Phil. Mag.*, 41, 1 (1896); also *Phil. Trans. A.*, 186, p. 216 (1895).

¶ *Phil. Mag.*, 41, 49 (1896).

APPARATUS NO. 1.

The fundamental principle of this method is the determination by condensation of the total heat of the vapour, and the subtraction from it of the total heat of the liquid to just below the boiling point.

This method was found to be extremely convenient, but suffers under the disadvantage that the accuracy attainable is determined by the relative magnitudes of the heat of evaporation and the specific heat of the liquid.

The experiment resolves itself into two parts (*a*) the determination of the total heat of the vapour, and (*b*) the determination of the mean specific heat.

The apparatus employed for the determination of the total heat of the vapour is illustrated in Fig. 1.

DESCRIPTION OF APPARATUS FOR TOTAL HEAT OF THE VAPOUR.

A continuous flow calorimeter was employed for the measurement of the heat liberated by the condensation of the vapour and the cooling of the fluid.

Referring to Fig. 1 the large vessel was wound with an external heating coil of approximate resistance 8 ohms, and through the top a thermocouple of copper-constantan projected, which recorded the temperature of the vapour.

To diminish any radiation transfer between the liquid and the top of the boiler, the conical metal shield shown in the figure was placed inside. This was perforated with holes to allow free circulation of the vapour, and supported on a sheet metal cylinder which stood in the vessel. The outside and top of the heater were well lagged with asbestos wool contained in a sheath of asbestos paper. A re-entrant brass tube passed through the base of the heater, and was of such length that it projected above the surface of the liquid. Through this tube was carried a silica tube, extending to about 20 in. below the base. This was surrounded with a water jacket through which a stream of water was passed at constant head. The water stream was arranged to flow up an outer jacket, when its temperature was approximately that of the air, and down the inner jacket, during which time it took up heat from the liquid, and was almost completely shielded from radiation by the surrounding stream of incoming water. As additional protection the tube was heavily lagged with cotton wool. A thermometer inserted in a U-tube in the pipe line gave the temperature of the water on its entrance to the apparatus, and a set of copper-constantan thermocouples arranged differentially gave the rise of temperature due to the heat absorption. A third thermocouple was inserted in the exit of the silica tube in such a way that the condensed liquid flowing down the latter ran over the junction.

Thus the experiment consisted in steadily boiling the liquid under examination by means of the heating coil, when the vapour produced escaped into the silica tube, and, flowing down this, was condensed; the heat given up in this process, and in cooling down to the temperature at which it was collected, is absorbed by the water flowing in the surrounding condenser. Hence, when a steady state is reached, we have, if Q is the water flowing per second, θ its rise (measured by the differential couples), t_2 and t_1 the temperature of the vapour and of the liquid at its exit from the apparatus, and L its latent heat, s its mean specific heat in the liquid form over the range t_2 to t_1 , and m the mass of liquid condensed per second.

$$Q\theta = m[L + s(t_2 - t_1)].$$

Here s is known from a separate experiment, and every other quantity is directly

measured. Q was determined by taking the time to fill a graduated flask, and it may be remarked that when the time measured was about 80 seconds the extremes of several successive determinations of Q differed by less than 0.6 second.

m was determined by collecting fractions for 30 seconds or 1 minute and weighing.

It will be noted that the value of s required is that over the range t_1 to t_2 (in

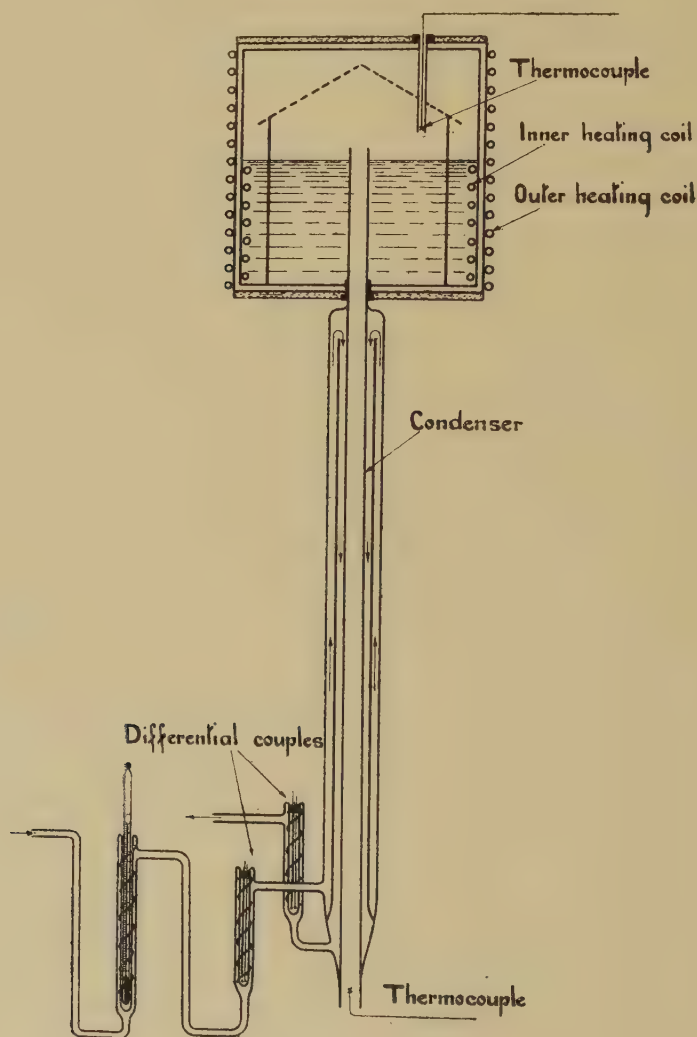


FIG. 1.

these experiments about 30°C. to 340°C.), whereas that found experimentally was determined over the range 20°C. to 320°C. approximately. It is not anticipated that the variation of specific heat with temperature is sufficiently large to introduce any appreciable error from this fact.

DESCRIPTION OF APPARATUS FOR THE SPECIFIC HEAT OF THE LIQUID.

The method of mixtures was adopted for this part of the experiment in the following form.

The liquid under test was heated in a thick copper vessel of about 750 c.c. capacity, which had a large bore gas cock silver-soldered in the bottom. This was well lagged with asbestos wool, and immediately before an experiment some liquid was run out, so that contact with the tap would not cool the sample used for the experiment. The vessel was wound with a heating coiling of nichrome strip, of about 4 ohms resistance cold, and this sufficed to heat the liquid inside from room temperature up to 350°C. in about an hour.

The temperature was obtained with a nitrogen filled mercury thermometer passed through a packing gland in the lid of the vessel. This thermometer was calibrated under the same conditions of immersion as those of the experiment.

PROCEDURE IN CARRYING OUT AN EXPERIMENT.

By means of the heating coil, the temperature of the liquid was raised to just below the boiling point. Some of the liquid was then run out so as to bring the temperature of the outlet pipe up to that of the liquid. Finally some of the liquid was rapidly run into the calorimeter. The fluid in the calorimeter was an oil whose specific heat at air temperature was determined by the customary methods.

RESULTS AND CHECK EXPERIMENTS.

The working of the apparatus was first tested by determining in it the latent heats of the following liquids, the values for which have previously been determined, and are quoted in the last column for comparison.

Substance.	Temp. of boiling °C.	s	$\frac{Q\theta}{m}$	$s(t_2 - t_1)$	L (cals. per gm.).	L (Kaye & Laby's tables).
Methyl alcohol	78.9	0.61	289	31	258	259
Water ...	100	1.00	605	68	537	540
Aniline ...	179	0.51	183	78	105	104

As the order of accuracy aimed at was only about 1 per cent. the agreement is satisfactory.

A further check on the apparatus was obtained by comparison with the results of an alternate method of experiment now to be described.

A SECOND METHOD OF USE OF APPARATUS I.

In this series of experiments the converse principle was applied, in that the heat required to evaporate a known mass of liquid was determined, instead of that liberated on condensation of vapour. To adapt the apparatus above described for this purpose another heating coil was wound on a mica cylinder and fixed inside the boiler, suitably insulated from the base and from the central brass pipe. It was of such dimensions that it was completely submerged in the liquid throughout an experiment.

The procedure adopted was to pass a suitable small current until a steady temperature was attained in the liquid, and to repeat this with several values of

the current until a curve could be drawn showing watts expended against temperature of equilibrium. When the liquid was at a steady temperature the energy supplied was lost by radiation from the surface of the calorimeter, and by a small graphical extrapolation over a range of about 20° or 30°C. the energy required to maintain the apparatus at the boiling point could be deduced.

In the next stage of the experiment the energy supply was increased considerably so that the liquid was boiling freely. The rate at which it distilled over was obtained by collecting fractions for a known time. In this method there is no question involved of total heat. The energy supplied, less that radiated, is all employed in vapourising the liquid, and hence the calculation of the heat of evaporation involves merely the measurement of the energy supply and the weight of liquid condensed.

One important precaution to be observed in these experiments was to maintain the conditions uniform throughout as regards the thickness of the lagging and the prevention of draughts.

A check experiment was carried out with aniline, and the results are shown below :—

Mass of aniline in 30 secs. (gms.)	Temperature. °C.	Total Energy Supplied.			Energy Radiated. (Cals.)	Energy entering aniline. (Cals.)	Heat of evaporation. (Cals. per gm.)	Remarks.
		(Volts.)	(Amps.)	Cals.)				
...	50	25.0	3.44	20.5	20.5	These figures were utilised for drawing the curve of radiation loss against temperature.
...	135	29.4	3.91	27.45	27.45	
...	140	29.6	3.92	27.7	27.7	
...	159	33.9	4.50	36.4	36.4	
17.88	183	57.16	7.51	102.6	40.8	61.8	103.7	The heat of evaporation is given in tables as 104.

ACCURACY OBTAINABLE.

The examples we have given above represent a rather higher degree of accuracy than we have been able to obtain in tests on certain commercial liquids, owing to the high fraction of the total heat which the specific heat term represented. In our experience it is the determination of the specific heat which is the more troublesome determination to make and the one which appears to be subject to the greater uncertainty.

Thus, for example, we have for one liquid $\frac{Q\theta}{m} = 261.3$, $s(t_2 - t_1) = 191.4$, whence $L = 69.9$. In this case, an error of 1 per cent. in the specific heat introduces an error of nearly 3 per cent. in latent heat.

Even for materials of low latent heat we consider that an equal accuracy would be attainable by means of the second method of using Apparatus No. 1 with an internal heating coil. This method, however, is slow, since the radiation correction

must be redetermined on each occasion that the lagging is disturbed, and this involves allowing the temperature to become steady at four or five points, each of which may take two to three hours.

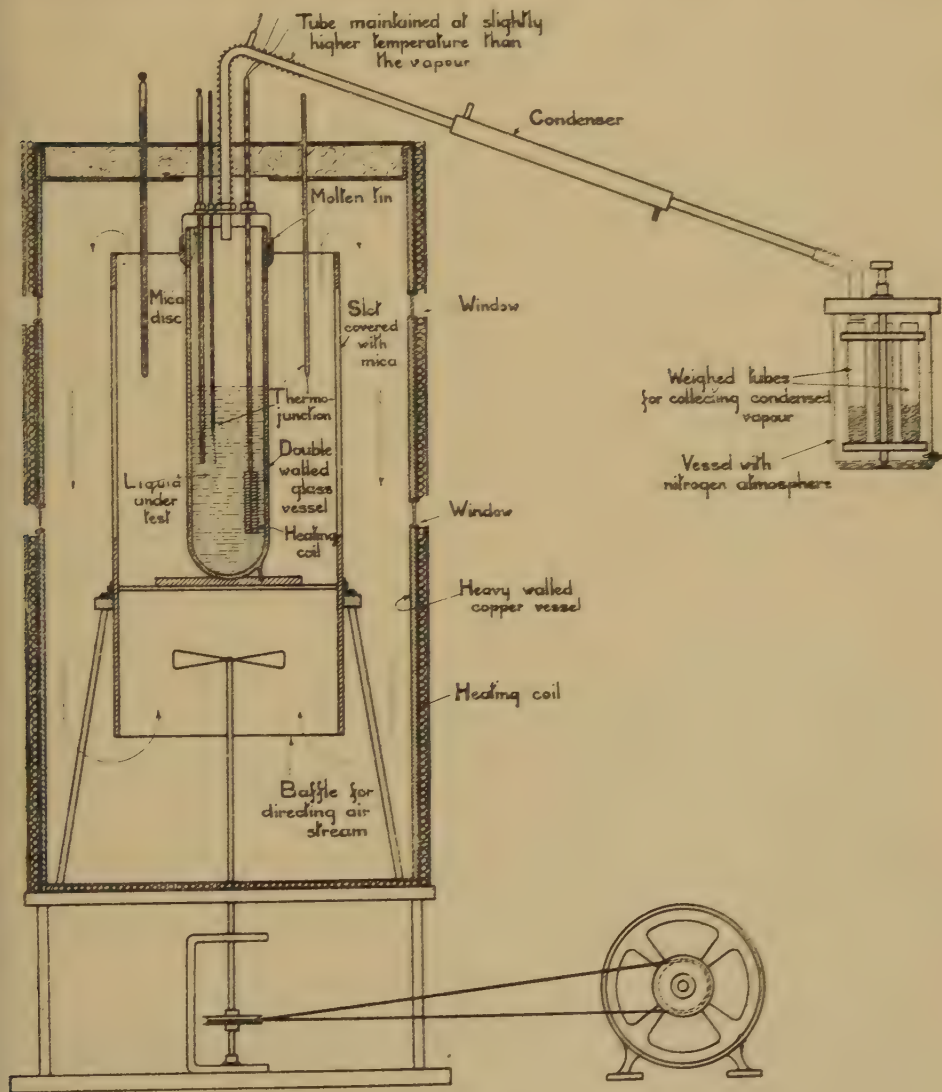


FIG. 2.

DESCRIPTION OF APPARATUS II.

The chief objection to the apparatus above described is the necessity for subsidiary experiments to determine either the specific heat of the liquid or the heat required to maintain the calorimeter at the temperature of the boiling point of the liquid.

An apparatus will now be described in which the heat of evaporation is determined directly, without any necessity for determining the total heat to the boiling point; in this respect it resembles the second method above described, but it is superior to that method in economy of time.

The principle was to hold the liquid at the boiling point, and then to measure the amount vapourised for a given further expenditure of energy. It is evident that this can only be done if the radiation losses are of negligible magnitude, and to secure this it was found possible to eliminate the radiation entirely by holding the surroundings at the same temperature as the liquid.

The apparatus is shown in Fig. 2. Its main features are a small double-walled vessel to contain the liquid under examination, provided with a condenser tube for the final collection of the condensed vapour. This vessel is closed by a pressed metal lid whose edge is submerged in a layer of molten tin. A well fitting disc of mica rests on the top edge of the double-walled vessel, so that a thermally insulating stopper is obtained. Surrounding the double-walled vessel is another thick walled metal enclosure wound with a heating coil, so that it can be maintained at the same temperature as the liquid. A shaft carrying a fan passes through the base of this, the function of the fan being to keep the air in motion, thereby insuring thermal uniformity within the apparatus. The liquid was heated by means of a submerged coil until the vapour was just slowly distilling over, and the outer jacket was then maintained at this temperature. Equality of temperature was obtained by observing the motion of a galvanometer spot in the circuit of a differential thermocouple with junctions on the wall and in the liquid. To secure uniformity of temperature, the air inside was kept in continual movement, baffle plates being arranged to direct its path all round the double-walled vessel.

Under these conditions, there could be but little radiation from the liquid outwards, and the residual effect was allowed for by determining the energy required to produce a very slow rate of evaporation. Hence a careful weighing of the amount vapourised per second at two known rates of energy input gave, by difference, a value for the heat of evaporation that was probably of a high order of accuracy.

It is, perhaps, worth while to point out to what extent the plan here employed to eliminate radiation losses may introduce uncertainty.

We have two cylindrical vessels, one inside the other, of radii a and b at temperatures which are supposed to be equal. Let us suppose, however, that there is an actual difference of 1°C . between them. The heat radiated from the inner will then be (assuming Stefan's Law)

$$2\pi a \times 1.374 \times 10^{-12} [(\theta+1)^4 - \theta^4]$$

$$= 11 \times 10^{-12} \pi a \theta^3 \text{ cal. per sec. per cm. of length.}$$

Thus, if the energy supply to the liquid is H cal. per sec. and the true latent heat L , we shall have

$$\frac{(H - 11 \times 10^{-12} \pi a \theta^3)}{L} \text{ gms.}$$

evaporated per sec. and we shall deduce a latent heat of

$$H - \frac{HL}{11 \times 10^{-12} \pi a \theta^3} = L \left[\frac{1 + 11 \times 10^{-12} \pi a \theta^3}{H} \right]$$

cal. per gm., which is in error by $\frac{11 \times 10^{-10} \pi a \theta^3}{H}$ per cent.

To see what this may mean let us take a few typical values.

$a=30$ cm.	$H=12$ cal. per sec.	$\theta=300^{\circ}\text{K.}=27^{\circ}\text{C.}$	Error $=0.23$ per cent.
„	$=50$ watts approx.	$=500^{\circ}\text{K.}=227^{\circ}\text{C.}$	„ $=0.55$ „
„	$=$ „ „	$=700^{\circ}\text{K.}=427^{\circ}\text{C.}$	„ $=1.08$ „
$a=300$ cm.	$H=200$ cal. per sec.	$\theta=300^{\circ}\text{K.}=27^{\circ}\text{C.}$	„ $=0.14$ „
	$=800$ watts approx.	$=500^{\circ}\text{K.}=227^{\circ}\text{C.}$	„ $=0.33$ „
		$=700^{\circ}\text{K.}=427^{\circ}\text{C.}$	„ $=0.65$ „

The above figures, which take account of radiation only, are merely illustrative, since they neglect convection, and, further, assume an emissivity of unity. Nevertheless, they illustrate the order of the error, as radiation is the important factor to be considered at high temperatures.

A source of practical difficulty in the manipulation lay in the necessity for using a "tin-seal" to close the top of the double-walled vessel. We were unable, however, to find any other convenient way of preventing the egress of vapour, so that we had to perform the filling of the seal on each occasion when the melting point of tin was reached (232°C.). In testing inflammable liquids the vapour was apt to take fire on coming into contact with the air in the tube, so that we had to have the end of the condenser tube and collect the condensate in an atmosphere of nitrogen.

Our best thanks are due to Mr. A. R. Challoner, of the Observer Staff, for very skilful assistance both in the construction of the various forms of apparatus and in the taking of observations with them.

DISCUSSION.

Mr. C. R. DARLING referred to the apparatus mentioned in the Paper as having been used by Sir William Ramsay and Miss Marshall. He had thought of using a modification of this apparatus for the absolute measurement of latent heat, the modification consisting in the use of a metal container for the liquid instead of a glass one, while the vapour would be led off by a side tube to a condenser. He had found that the temperature of the liquid under measurement would differ in such circumstances by only a degree from that of the similar liquid in the surrounding jacket. Did the authors see any serious objection to this proposal?

Mr. J. H. BRINKWORTH described experiments on the latent heat of steam which he had made some years ago, at the suggestion of Prof. Callendar, the water under test being jacketed by its own vapour. He had hoped to attain an accuracy of $1/10$ per cent., but had concluded that the results fell short of this standard in consequence of (1) heat conduction along the leads of the heating coil, and (2) priming, or the carrying over of particles of unevaporated water with the steam. Had the authors considered these sources of error?

Mr. F. E. SMITH remarked that the expression "latent heat of a liquid" is an incorrect one: it is preferable to speak of the latent heat of a vapour.* An idea which he had once had for the accurate determination of J now suggested to him a different method of using the apparatus, shown in Fig. 1 of the Paper. If the liquid in the upper container were kept at its boiling points assumed constant, its rate of evaporation could be altered by altering the current in the heating coil, radiation conditions being unaffected, because the temperature would be unchanged. At the same time, by altering the rate of flow of the water in the condensing jacket the temperature there could be kept constant, so that the rates of evaporation for two different heating currents could be found under precisely the same radiation conditions, and hence the latent heat could be calculated. The principal sources of error should, apparently, be capable of being eliminated by this process.

Dr. E. GRIFFITHS, replying to the discussion, said that the apparatus of Ramsay and Marshall

* Amendments were subsequently made in the Paper to meet this criticism.—EDITOR.

was certainly one of the prettiest which had been devised for latent heat determinations and was suitable for use in connection with pure liquids. A defect of the apparatus was the error due to the evaporation of the liquid in the period of heating up to the boiling point and before the electrical energy had been switched on. This, of course, could be overcome by slightly modifying the apparatus so as to collect the distillate during the period of the electrical supply.

It will be remembered that Ramsay and Marshall arranged their apparatus in duplicate because at that time methods of measuring heat as electrical energy had not been brought to the high degree of perfection that pertains at the present day. It would probably be advisable to measure the heat by observations of the watts dissipated in the coil. As regards the present apparatus, the authors had had commercial liquids in mind and in that case the boiling point might be rather indefinite owing to impurity or to "cracking." One of the present apparatus resembled that of Ramsay and Marshall, but had been designed so as to offer the maximum thermal resistance to heat conduction between the container and the jacket.

An unsolved problem in this connection is that of making an effective heat insulating stopper which will stand a temperature of 350 to 450°C. In the form of apparatus described by Ramsay and Marshall the question of radiation needs consideration; for example, a platinum thermometer in vapour of boiling sulphur may register a temperature half a degree less than the true temperature on account of radiation and of condensed vapour running down it.

Priming presents a very serious difficulty, and it is mainly on that account that an accuracy of only 1 per cent. is claimed in the present Paper. It should be possible, however, to so modify the apparatus that by means of a subsidiary heating coil the vapour coming off is definitely superheated and thus any heat required for the evaporation of minute globules would be taken account of. This, of course, would necessitate a knowledge of the specific heat of the vapour.

The President's suggestion was a valuable one, but apparently errors due to priming would not be entirely eliminated by the proposed method of working.

XXI.—ON THE STUDY OF DIFFUSION IN LIQUIDS BY AN OPTICAL METHOD.

By BASIL W. CLACK, *M.Sc., Ph.D., F.Inst.P.*, Lecturer in Physics at Birkbeck College.

Received March 11, 1924.

ABSTRACT.

This Paper describes experiments carried out in the steady state of diffusion, by means of which the coefficient is measured by the deviation of an incident horizontal pencil of light, which traverses the solution under investigation at different depths below its surface. The concentration of the solution varies with the depth from zero to complete saturation, but is constant with the time, and the accuracy in measurement is increased by the employment of interference fringes. The coefficient of diffusion, in certain cases, is found to pass through a minimum value, in accordance with the expectations of Arrhenius, increasing for more dilute solutions towards Nernst's theoretical limit. In general, the author's earlier investigations are confirmed.

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- § 2. Theory.
- § 3. The diffusion cell.

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- § 4. Determination of rate of change in mass of cell-contents.

SECTION B.

- § 5. Determination of $[d\mu/dl]$.
- § 6. Optical arrangements.
- § 7. Determination of h .

SECTION C.

- § 8. Interferometer results for $[d\mu/dn]$.

SECTION D.

- § 9. Distribution of concentration along the tube.
- § 10. Results for Diffusivity.
- § 11. Study of dilute solutions.
- § 12. Conclusion.

§ 1. INTRODUCTION.

THE subject of Diffusion in Liquids has hitherto been studied by the author by a gravimetric method,* in which flasks of a special design, filled with the solutions under investigation, were suspended from the arms of a delicate balance,

* See Clack: "On the Coefficient of Diffusion," *Proc. Phys. Soc. Lond.*, Vol. 21, p. 863, (1908). "On the Temperature Coefficient of Diffusion," *Proc. Phys. Soc. Lond.*, Vol. 24, p. 40 (1911). "On Diffusion in Dilute Solutions," *Proc. Phys. Soc. Lond.*, Vol. 27, p. 56 (1914). "On Diffusion in Liquids," *Proc. Phys. Soc. Lond.*, Vol. 29, p. 49 (1916). "On Diffusion in Saturated Solutions," *Proc. Phys. Soc. Lond.*, Vol. 33, p. 259 (1921). "A Research on Diffusion in Liquids," *Ph.D. Thesis* (1922).

so as to hang immersed in a large bath of distilled water maintained at various constant temperatures by means of a thermostat. It has been shown that the value of the diffusivity of the solutions can be obtained from the final steady rate at which the flasks changed their weight. Although satisfactory and consistent results have been obtained by this method, yet it suffers from three defects :—

(1) The accuracy diminishes at low concentrations, and errors of 5 per cent. or more may be found for weak solutions.

(2) The value of the coefficient obtained is a kind of mean value over a range of concentration.

The author has shown that it is possible, since the steady state of diffusion has always been employed, to deduce theoretically from these "mean" diffusivities, the actual value of the coefficient at any definite concentration (*loc. cit.*, 1916, 1921, 1922), yet it would appear more desirable to obtain this quantity by direct experiment.

(3) A large number of separate experiments are necessary in order to study the phenomena over the whole range of concentration from very dilute solutions

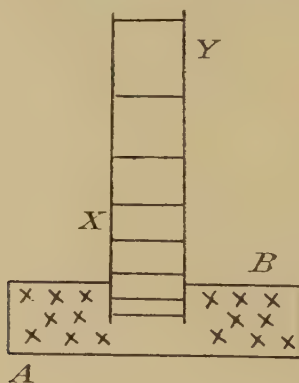


FIG. 1.

up to complete saturation. This necessitates a very large expenditure of time in order to complete the investigation of each salt.

The object of the present Paper is to describe an optical method by which these defects are avoided, and in which the results, obtained in the steady state, give at once the coefficient of diffusion at any definite concentration directly; and in which all concentrations of the aqueous solution of the salt under examination are investigated in a single experiment, so that a considerable economy in time is effected.

The experimental values obtained by this optical method are then to be compared with those indirectly computed from the earlier investigations.

§ 2. THEORY.

Consider a uniform vertical tube, XY (Fig. 1) initially filled with a saturated solution of the salt under investigation, and so arranged, by methods to be explained later, that its upper end may be maintained in contact with either pure water, or

ternatively, a solution of constant and very feeble concentration; and further, it is assumed that the lower end of the tube is simultaneously kept in contact with a saturated solution of the salt to be examined, by providing it with a shallow compartment, *AB*, which contains crystals of the salt.

Under these conditions the author has shown (Proc. Phys. Soc. Lond., Vol. 29, 1916) that in a diffusion tube of unit cross-section, if

n = concentration of the solution in gms./c.c. at a point l cm. below the top of the diffusion tube, when the steady state has been reached.

d = density of the solution at the same point.

i = change in mass of cell-contents per second when the steady state has been reached.

δ = ratio of the mass of water which enters the top of the diffusion tube to the mass of salt c , leaving it per second, when the steady state has been attained.

K_n = coefficient of diffusion of a solution of concentration n .

$$\text{Then } K_n = [i/(1-\delta)] [dl/dn] [(d-n+n\delta)/(d-n)] \quad \dots \quad (1)$$

for a diffusion tube of cross-section A sq. cm.

$$K_n = [i/(1-\delta)A] [dl/d\mu] [d\mu/dn] [(d-n+n\delta)/(d-n)] \quad \dots \quad (2)$$

where μ represents the refractive index of the solution at a point l cm. below the top of the tube, for light of wave-length λ . Moreover it has been shown (Proc. Phys. Soc. Lond., Vol. 33, p. 262, 1921) that δ can be determined from the known values of the concentration and density of the saturated solution, and the density of the salt crystals; so that the coefficient of diffusion K_n at any definite concentration n can be determined by means of equation (2), from a knowledge of the four quantities included in the square brackets, viz. :—

A. The change, i , in the mass of the contents of the cell per second when the steady state has been reached.

B. The rate of change of the refractive index μ of the solution with the distance down the tube, in the steady state of diffusion.

C. The rate of change of the refractive index μ with the concentration n , for the various salt solutions investigated.

D. The density d , and the concentration n , at any point l cm. down the tube, when the steady state has been reached.

The methods employed in the determination of these four factors are discussed respectively in the corresponding sections **A, B, C, D**, following—viz., §§ 4, 5, 8 and 9.

§ 3. THE DIFFUSION CELL.

The diffusion cell, represented diagrammatically in Fig. 1, contains a diffusion tube *XY*, which has a height of 5.04 cm., and is rectangular in cross-section, having a width of 1.0025 cm. in the plane of the diagram (Fig. 1), and a depth of 4.21 cm. at right angles to this plane. It is made of glass plates cemented together with zinc oxide and water-glass cement, and is fitted at its lower end into a shallow glass box

AB , about 4 cm. square, and 1 cm. high. The whole of this apparatus is filled with air-free saturated solution, and the concentration of the solution at the lower end of the rectangular diffusion tube is maintained constantly at complete saturation by supplying the shallow box AB , with crystals of the salt under test.

Preliminary Series.

In a preliminary series of experiments, the diffusion cell, filled as described above, was suspended from one arm of a balance by a fine platinum wire, so as to hang immersed in a large tank containing 30 litres of distilled water which was maintained at a constant temperature by thermostatic means, and observations were made of the weight of the cell every day. The volume of water in the tank was so large that the concentration at the upper end of the diffusion tube may be considered to be always zero, and under these conditions diffusion proceeds, and after about 12 days a steady state is reached, in which the cell decreases in weight by the same amount every day, so that, if i_0 be the rate of change in the mass of the cell-contents under

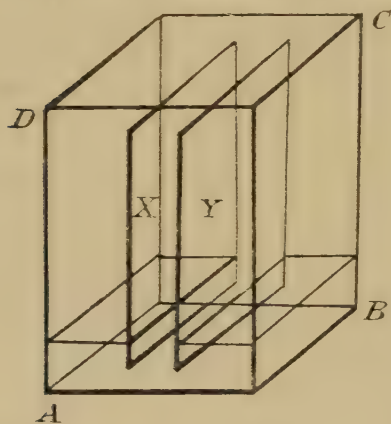


FIG. 2A.

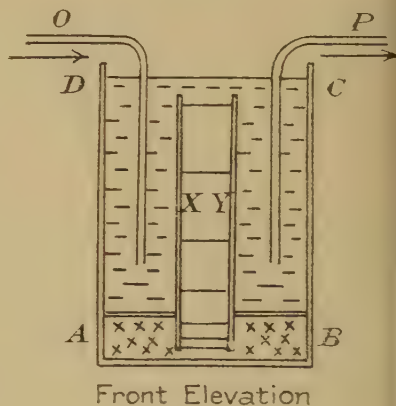


FIG. 2B.

the circumstances mentioned, i_0 becomes constant, having the values included in Table I.

Further particulars of these preliminary experiments will be found in Proc. Phys. Soc. Lond., Vol. 33, p. 263 (1921), and their application to the present investigation will be explained in the paragraph, § 4.

Main Series of Experiments.

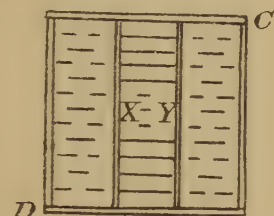
In the main series of optical experiments to be described in the present Paper, however, the use of a large tank was attended with difficulties, and the steady state was accordingly brought about in a different manner, which necessitated the following modification in the construction of the cell.

The same diffusion cell was employed, but the shallow glass box AB (Fig. 1) was extended upwards as suggested in Figs. 2A and 2B, so as to enclose the diffusion tube XY on both sides, and to rise about 1 cm. above the top of it. The glass plates X and Y , which form the sides of the diffusion tube extend completely from the front to the back of the cell (see Fig. 2c), but, as will be seen indicated in Figs. 2a

and 2B, they do not reach quite to the top or to the bottom of the external cell *ABCD*.

The outer parts of the cell, between the plate *X* and the wall *AD* (Figs. 2A, 2B), and between the plate *Y* and the wall *BC*, are filled with distilled water, which also rises about 5 mm. above the top of the diffusion tube *XY*, and a slow steady current of distilled water of about 50 c.c. per day is maintained through the cell, as indicated by the arrows in Fig. 2B.

In about 12 days after the flow has been commenced, the approximately steady



Plan.

FIG. 2C.

state is reached, in which the water-current removes the salt as fast as it diffuses up the space between the plates *X* and *Y*, and the concentration of the solution at the top reaches a constant calculable value, only slightly greater than zero, and the concentration at each point of the tube *XY* continues constant in time, remaining

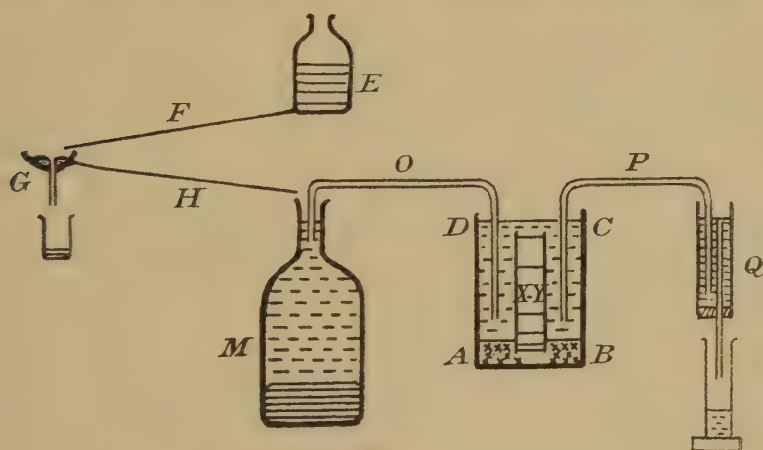


FIG. 3.

is always saturated at the bottom by reason of the presence of the salt crystals in the compartment *AB*.

The arrangements for producing the slow constant flow of water over the top of the diffusion tube *XY* are suggested in Fig. 3. A reservoir, *E*, contains mercury (which must be replenished every day), which flows through a fine capillary tube, *F*, about 1 metre long, falling in tiny droplets into the constant-level reservoir *G*. This

of the liquid at the top of the diffusion tube. Then N' can be obtained by direct chemical analysis of the solution flowing out of the cell. For example, in the case of the chlorides, using a few drops of potassium chromate as indicator, the solution was titrated against deci-normal silver nitrate with the results included in Table I. below.

In other cases the value of N' was estimated by the evaporation of a known volume of the liquid collected at the exit-tube Q (Fig. 3) in a platinum dish over a water-bath at 100°C ., the residue being then dried in a vacuum desiccator and weighed.

There is, however, no need to make a direct analysis, in order to obtain the concentration N' of the solution flowing out of the cell, and the author has preferred another method of finding its value, which does not require the special experience necessary for exact results in chemical analysis, and he regards the analyses as providing a check on the accuracy of this method. The value of N' has accordingly been obtained from the results of the preliminary gravimetric experiments in which the large tank was used in the following manner:—

Let q = constant volume of dilute solution flowing out of the cell per unit of time.

Then in the steady state

$$N'q = c = i/(1-\delta) \quad \dots \dots \dots (4)$$

or, to a sufficiently close approximation

$$N_0 = i_0(N - N_0)/(1-\delta)qN.$$

The values of the concentrations N_0 thus obtained are given below, and from these figures the rate of change i in the mass of the contents of the cell per unit of time is calculated by means of Equation 3. The summarised results are collected in Table I.

TABLE I.

Salt.	K Cl.	Na Cl.	K NO ₃
N gms./c.c.	0.29956	0.31813	0.26001
N' gms./c.c.	0.00626	0.00546	...
N_0 gms./c.c.	0.00619	0.00543	0.00376
i gms./day	0.1652	0.1460	0.1099
i_0 gms./day	0.1687	0.1486	0.1115
q c.c./day	56	52	57
δ	0.5236	0.4827	0.4878

It may be observed that the values of i given above have been deduced by the aid of Equation 3, and not from Equation 4, because the results obtained from the latter equation are found to be liable to greater inconsistency. It should be noted that N_0 is small, and an inspection of Equation 3 will show that relatively large errors in the estimation of its value will produce negligible effects in the value obtained for i ; in fact, it is only necessary to know N_0 with any considerable accuracy when it is required to find the coefficient of diffusion for extremely weak solutions.

SECTION B.

§ 5. DETERMINATION OF $[d\mu/dl]$.

In order to find the value of $[d\mu/dl]$, i.e., the rate at which the refractive index of the solution changes as we pass down the cell, a horizontal pencil of light is passed through the cell from back to front so as to traverse the 4.21 cm. depth of the solution between the glass plates X and Y at right angles to the plane of the Figs. 2B and 3. The beam emerges from the front of the cell deviated from its original incident horizontal path through an angle α , which varies with the distance l of the point of incidence of the incident ray from the top of the diffusion tube. As the incident pencil is allowed to fall upon the back of the cell at different depths below the surface of the liquid, the resulting angle of emergence α , measured from the horizontal, is observed, and from these values of α for different values of l it is possible to determine the quantity $d\mu/dl$. Consider the passage of a ray of light AB (Fig. 4), incident horizontally at A on a glass cell filled with the aqueous solution of a salt whose concentration is maintained at complete saturation at the bottom of the cell, and

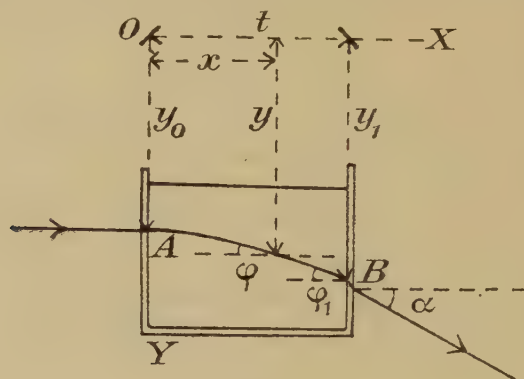


FIG. 4.

at approximately zero concentration at the top, as in the experiments carried out in this investigation. After sufficient time has elapsed and the steady state of concentration has been established in the cell, the concentration at each depth will remain constant, and under these circumstances the path of the ray through the cell is readily investigated, and it can be shown that $\mu_0 = \mu \cos \phi$, where μ_0 is the refractive index of the solution at A , and μ and ϕ refer to any point on the ray whose co-ordinates are x and y . (See Fig. 4.)

If we take the origin O at such a point that $\mu = \mu' y$, where $\mu' = d\mu/dl = \text{constant}$ over the small range of concentration traversed by the ray AB , then

$$dy/dx = \tan \phi = \sqrt{\mu^2 - \mu_0^2} / \mu_0 = \sqrt{y^2 - y_0^2} / y_0,$$

whence

$$y = y_0 \cosh x/y_0,$$

so that the path of the ray is a catenary.

Considering the refraction through the glass at B , it can be shown that \sin

$=\mu' y_0 \sinh t/\gamma_0 = \mu' t$ approximately, where t indicates the thickness of the cell traversed by the ray—i.e., 4.21 cm. Whence

[illegible]

§ 6. OPTICAL ARRANGEMENTS.

The diagram (Fig. 5), which is a side elevation of the apparatus, gives a general idea of the optical arrangements employed. The quartz mercury arc A is focused by means of a lens L_1 and a plane mirror M , so as to illuminate the horizontal slit S_1 of the Hilger constant deviation spectroscope L_2PL_3 , which is set up so that the axis of rotation of the prism is horizontal. The dispersed images of the slit S_1 are focused by the lens L_3 on to a screen S_2 , and the green mercury line ($\lambda=5461$) is arranged to

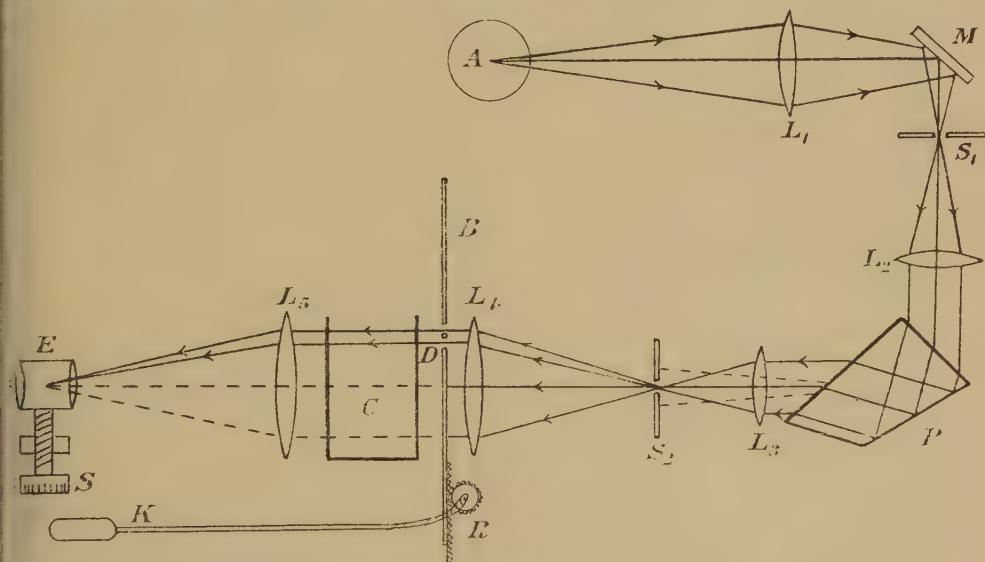


FIG. 5.

fall on a very fine horizontal slit contained in this screen, the other radiations being intercepted by S_2 .

The green light, diverging from the slit S_2 , is incident on a lens L_4 of focal length about 1 metre and aperture 12 cm., placed at a distance equal to its focal length from the slit S_2 . The emergent parallel beam, after traversing the diffusion cell C (Fig. 5) in a direction at right angles to the plane of the paper in Figs. 2B and 3, and is converged by a lens L_5 of similar focal length and aperture, on to the eyepiece E , fitted with fine cross-wires at 45° to the horizontal and capable of being moved in a vertical direction by the screw S of $\frac{1}{2}$ mm. pitch, whose head is divided into 100 parts. In order to allow the light to be passed through the cell at different depths below the surface, another screen B , containing a suitably arranged aperture D , is placed in the position shown, and is capable of movement in a vertical plane by means of a rack and pinion R , and a flexible shatting which can be rotated by the knob K , operated by the observer at the eyepiece. This screen is provided with a

scale and vernier, by means of which it is possible to ascertain the depth l below the upper end of the diffusion tube, of the incident ray of light which passes through the aperture D . A narrow horizontal slit could not be utilised for the aperture D , as it was found that owing to diffraction effects no definite image could be observed in the eyepiece with such an aperture. On widening the slit at D it was found that a sufficiently sharp image of the slit S_2 could only be obtained when the vertical width of the aperture D was 6 mm. or more; but even then only when the cell was filled with a solution of uniform density. Under the conditions of the diffusion experiment, the variation of the refractive index of the solution within the range of depth of 6 mm., when the steady state had been reached, was again sufficient to destroy all sharpness in the image observed. It was accordingly decided to use for the aperture D two narrow horizontal slits close together, thus producing horizontal interference fringes which can be observed in the eyepiece E .

But to measure the angle of emergence α (Fig. 4) it is necessary always to record the position of the same fringe in the eyepiece by means of the screw S . It is not possible in the present case to identify a particular fringe by employing the common device of making observations on the achromatic fringe in white light, for as the aperture D is lowered from the position $l=0$ to $l=5$ cm. the achromatic fringe moves rapidly upwards, moving relatively to the interference fringes, which remain almost stationary. The achromatic fringe and the aperture D always lie on opposite sides of the optic axis of the lens L_5 (Fig. 5), and the ratio of their distances from it appears to be approximately constant.

Owing to this great relative movement between the interference fringes observed in white light, and the achromatic fringe, when the aperture D (Fig. 5) was moved in a vertical plane, it was found to be inconvenient to attempt to identify a particular fringe by means of the position of the achromatic fringe, and this method was not proceeded with. It was finally decided to make the width of the two horizontal slits in the screen B (Fig. 5) and their distance apart of such magnitudes as to produce only a very limited number of green mercury fringes visible in the eyepiece, when it is not difficult to select always the same fringe for observation.

The slits were made by removing the silver deposited on a plate of glass by means of a special chisel ground for the purpose from a hack-saw blade, and from a number of pairs of slits thus produced those were selected for the research which appeared on trial to give the best and clearest fringes.

Most of the experiments to be described were made using two slits each about $\frac{1}{4}$ mm. wide and about 1.3 mm. apart between corresponding points. As is well known, the field in the eyepiece will be crossed by two sets of lines—the interference fringes, in the same position as those due to two point sources at a distance 1.3 mm. apart, and the diffraction fringes due to each aperture, and the resulting intensity in the field of view is such that, with the dimensions given above, only 9 well-separated fringes could be seen in the eyepiece. (See, for example, Wood's Physical Optics, p. 202.) If the slits are put closer together, the interference fringes are proportionally coarser, and therefore less accurate as fiducial marks. If further apart, the fringes are finer, but not so satisfactory on account of the greater length of the element of the diffusion tube experimented upon. Similarly, the width of each slit affects the total number of lines visible, and compromise is necessary. The result of actual trial led to the selection of the slits mentioned as most satisfactory. The position of the central fringe of the nine visible in the eyepiece was

always recorded as the fiducial mark, the method of procedure being as recorded in the next paragraph. There was never any difficulty in deciding which was the central fringe, and only quite ordinary care was necessary.

§ 7. DETERMINATION OF h .

Commence with the aperture D in the screen B (Fig. 5) as high as possible and slowly lower it by the knob K . At a certain position the fringes suddenly appear in the eyepiece. The reading on the scale attached to B is taken to the nearest $\frac{1}{10}$ mm.; the cross-wires in the eyepiece are set on the central fringe of the nine in the field of view, and the reading of the screw S is taken to the nearest $\frac{1}{100}$ mm. The knob K is then turned, lowering the aperture D , until a counted number of fringes (say, three) cross the intersection of the cross-wires, say, upwards. The eyepiece is then raised by the screw S so that the cross-wire passes over the three fringes referred to, and is set once more on the central fringe. New readings are taken of the scale reading on B and of the screw S . This process is repeated until the aperture D reaches the bottom of the cell, and the fringes disappear.

By these means we procure that the eyepiece is successively raised by equal amounts (three fringe-widths), and when in each of its positions, the aperture D is moved by such an amount as to cause the fiducial fringe to coincide again with the cross-wire of the eyepiece. The necessary successive alterations of the position of D will not, in general, be equal. It may be mentioned that as the aperture D is lowered in the manner just described, it is found that the interference fringes seen in the eyepiece move continually upwards in the cases of solutions of KCl and NaCl in the steady state of diffusion; i.e., as l increases from zero to 5 cm., the angle α continually decreases in magnitude in the cases of these solutions. In the case of solutions of KNO_3 , however, the movement is less simple—as the aperture D moves downwards from the value $l=0$ to about $l=4$ cm. the angle α increases in magnitude. From $l=4$ to $l=5$ cm. the value of α remains approximately constant, or even slightly decreases. The whole movement in the case of KNO_3 is much less than that observed in solutions of NaCl or KCl (see Fig. 6). After readings have been taken in the manner described above for several days, and the substantial agreement observed satisfies us that the steady state has been attained with sufficient approximation (this occurs about 12-14 days after commencing the water-flow in the apparatus used in this investigation), the cell is repeatedly washed out with distilled water, so as to remove all trace of salt, without, however, disturbing in the least the position of the cell. Similar readings are then taken with the cell full of distilled water, in order to obtain the zero position of the eyepiece. That is to say, the aperture D is lowered as before and corresponding readings are tabulated of its position and of that of the eyepiece. During the whole 5 cm. range of movement of the aperture D the eyepiece will now only require to be moved quite a small amount, due to the want of optical perfection in the cell itself. Thus the zero position of the central fringe seen in the field of view of the eyepiece is not perfectly constant, but depends slightly on the value of l , that is, on the part of the cell traversed by the ray.

The difference between the position of the eyepiece during the main experiment and its zero position taken as just described will give the quantity represented by h .

such that $\tan \alpha = h/F$, where F is the focal length of the lens L_5 (Fig. 5), and hence approximately from Equation 5,

$$d\mu/dl = h/F \times t \quad \dots \dots \dots (5a)$$

where t is the thickness of the liquid traversed by the ray, and is equal to 4.21 cm., and $(d\mu/dl)$ represents the rate at which the refractive index of the solution for green mercury light changes as we pass down the diffusion tube.

Hence the determination of $(d\mu/dl)$ merely involves a measurement of h , the position of the eyepiece in the focal plane of the lens L_5 (Fig. 5).

In order to economise space, the complete records are not tabulated for all the experiments performed, but the results of the investigations made on solutions of NaCl are given graphically in Curves 1 and 2, Fig. 6; Curves 3 and 4 show the results of observations made on KCl; and Curves 5 and 6 indicate the results of experiments performed on KNO_3 .

From these graphs (Fig. 6) the following tables can be constructed, giving the mean values of h from the experimental observations on the salts referred to, when the steady state of diffusion has been attained.

TABLE II.

Na Cl.			K Cl.		KNO_3 .	
l	h_1	h_2	h_3	h_4	h_5	h_6
0.0	4.650	4.571	3.590	3.560	1.620	1.638
0.1	4.618	4.535	3.553	3.514	1.628	1.645
0.2	4.582	4.507	3.518	3.479	1.638	1.655
0.5	4.480	4.405	3.410	3.376	1.656	1.675
1.0	4.316	4.243	3.242	3.220	1.688	1.714
1.5	4.153	4.090	3.091	3.085	1.719	1.752
2.0	4.001	3.948	2.957	2.966	1.756	1.793
2.5	3.860	3.812	2.840	2.854	1.796	1.838
3.0	3.738	3.693	2.722	2.747	1.837	1.881
3.5	3.630	3.600	2.616	2.645	1.883	1.931
4.0	3.539	3.530	2.521	2.550	1.928	1.975
4.5	3.461	3.480	2.442	2.462	1.963	1.990
5.0	3.405	3.447	2.380	2.385	1.958	1.970

(Note.— h_1, h_2 , &c., refer to the corresponding number of the Graph Fig. 6.)

SECTION C.

§ 8. DETERMINATION OF $[d\mu/dn]$.

The third quantity whose value is necessary in order to determine the Coefficient of Diffusion is the rate of variation of the refractive index of the solution with respect to its concentration. This was studied by means of an interferometer of the type due to Lord Rayleigh (Proc. Roy. Soc., Vol. 59, p. 202, 1896).

The method of procedure was to place successively in the Hilger double cell a number of pairs of solutions of known and slightly different concentration, dn , and to measure the difference $d\mu$ in their refractive index.

The author hopes to submit to the Physical Society a further Paper on this work, and on the corrections involved in the interpretation of the results, so as to give $d\mu$ in terms of the green mercury light used in the experiments already

described in this Paper, and contents himself at present in giving a summary of these results in Table III.

TABLE III

Salt.	n_1	n_2	Mean. n	$d\mu/dn$
NaCl	0.2500	0.2273	0.239	0.1396
	0.1667	0.1488	0.158	0.1473
	0.1250	0.1042	0.115	0.1522
	0.0625	0.0446	0.053	0.1596
	0.0250	0.0125	0.019	0.1682
	0.0125	0.0000	0.006	0.1753
KCl	0.2500	0.2273	0.239	0.1111
	0.1667	0.1488	0.158	0.1153
	0.1250	0.1042	0.115	0.1189
	0.0625	0.0446	0.053	0.1243
	0.0250	0.0000	0.0125	0.1322
	0.0125	0.0000	0.006	0.1369
KNO ₃	0.2500	0.2273	0.239	0.08090
	0.1667	0.1389	0.153	0.08200
	0.1250	0.0893	0.107	0.08387
	0.0625	0.0312	0.047	0.08761
	0.0312	0.000	0.0156	0.09208
	0.025	0.000	0.0125	0.09255

These figures are plotted graphically on the curves of Fig. 7.

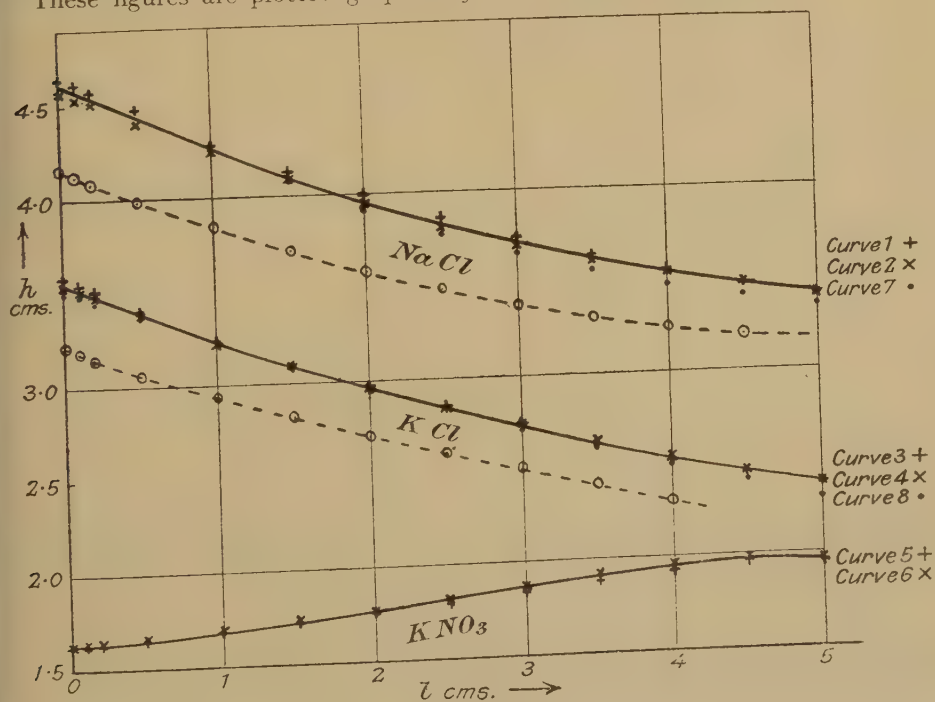


FIG. 6.

SECTION D.

§ 9. DETERMINATION OF THE CONCENTRATION AT ANY POINT OF THE TUBE.

As will be observed from Table III., $d\mu/dn$ is not constant for different values of n , and in order to find what value of it should be employed, as well as to estimate the factor $(d-n+n\delta)/(d-n)$, both of which quantities appear in Equation 2 as required in the calculation of the Coefficient of Diffusion, it is necessary to ascertain

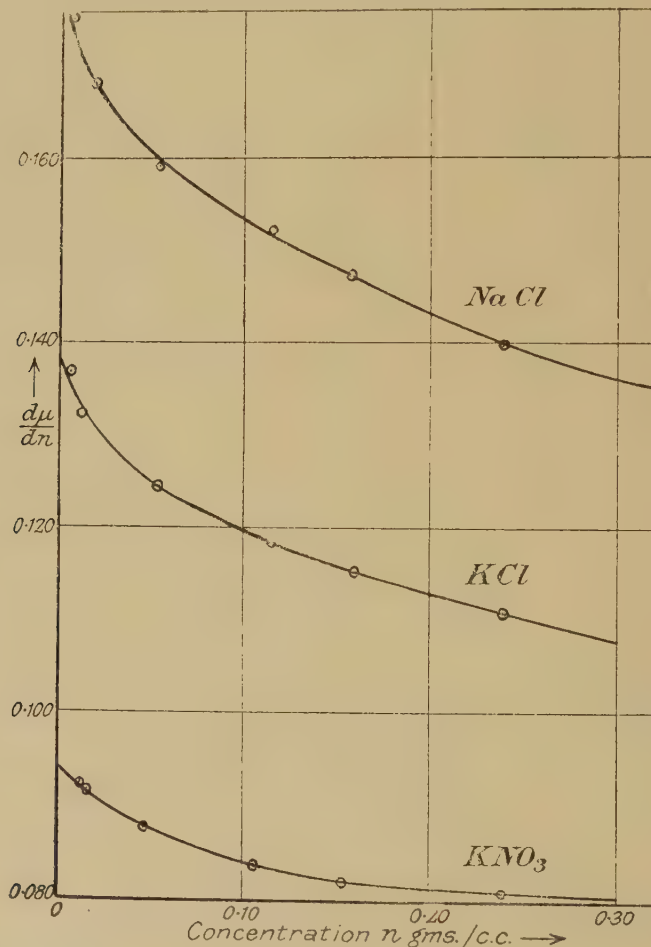


FIG. 7.

the concentration, n , when the steady state has been attained, of the solution at any point, l , selected in the diffusion tube. This distribution of concentration may be obtained by the following method :—

$$K_n = c[(d-n+n\delta)/(d-n)] [dl/d\mu] [d\mu/dn] \quad \dots \dots (2)$$

Now $[d\mu/dl]$ has been found experimentally for different values of l . (See Equation 5a, also Table II. and Graph Fig. 6.)

The function $[d\mu/dl]$ is plotted against l as abscissa, and the total area of the

curve between the ordinates at the origin and at L is measured, where L denotes the total length of the diffusion tube.

Now,
$$\int_0^L (d\mu/dl)dl = \mu_N - \mu_{N_0} \quad (6)$$

where μ_N is the refractive index of the saturated solution present at the bottom of the tube, at the point where $l=L$; and μ_{N_0} that of the very dilute solution at the top of the tube, where $l=0$. But μ_N and μ_{N_0} can be found from the results of the researches of Bender (Wied. Ann., 1890-1892) and Wagner ("On the Dipping Refractometer") published in Landolt and Börnstein's Tables, interpolation for the green mercury line $\lambda=5,461$ being made by means of Cauchy's Formula. Thus we obtain:—

K Cl.	Na Cl.	KNO ₃ .
$\mu_N = 1.3694$	1.3823	1.3568
$\mu_{N_0} = 1.3354$	1.3355	1.3352

Hence Equation 6 serves as a means of checking the accuracy of the graph, and it was found that a small difference existed between the total area of the curve between the limits mentioned, and the value of $(\mu_N - \mu_{N_0})$ given above. The exact method of applying a correction is necessarily somewhat uncertain, but this is not a serious matter, as the amount involved is small (one or two-tenths of 1 per cent.), and, from considerations of the method employed in the experimental measurements of $[d\mu/dl]$, it was decided that it would be most reasonable to amend all the ordinates by a constant amount.

The area of the corrected graph was then found between the zero ordinate and that at various selected values of the abscissa l .

Thus was determined graphically the value of the integral

$$\int_0^l (d\mu/dl)dl = \mu_n - \mu_{N_0} \quad (7)$$

where μ_n represents the refractive index of the solution of concentration n present in the diffusion tube at a point l cm. from the top of the tube.

Knowing μ_{N_0} , we thus find μ_n in terms of l .

TABLE IV.

	K Cl.	Na Cl.	KNO ₃ .
l_{cm}	μ_n	μ_n	μ_n
0.0	1.3354	1.3356	1.3352
0.1	1.3362	1.3367	1.3357
0.2	1.3371	1.3378	1.3360
0.5	1.3395	1.3410	1.3371
1.0	1.3435	1.3462	1.3391
1.5	1.3472	1.3513	1.3412
2.0	1.3508	1.3562	1.3432
2.5	1.3542	1.3608	1.3454
3.0	1.3575	1.3654	1.3476
3.5	1.3606	1.3698	1.3498
4.0	1.3636	1.3740	1.3521
4.5	1.3666	1.3782	1.3545
5.0	1.3694	1.3823	1.3568

Again, $[d\mu/dn]$ has been experimentally determined by the interferometer for various values of n . (See Table III. and Graphs Fig. 7.)

The function $[d\mu/dn]$ is plotted against n as abscissa, and the total area of this curve is measured, between the ordinates at the origin, and at N , where N , as before, denotes the concentration of the saturated solution.

Now,

$$\int_0^N (d\mu/dn) dn = \mu_N - \mu_w \quad \dots \dots \dots (8)$$

where μ_w represents the refractive index of pure water at 18°C. for light of wavelength $\lambda=5,461 \text{ \AA}$.

The total area of the curve between these ordinates is therefore known, and if necessary a small correction can be applied, as before, to the observed graph in order to satisfy Equation 8 exactly. This correction was always small, and again a consideration of the method employed in the measurement of $[d\mu/dn]$ indicates that the correction should probably be a constant one for all the ordinates. The area of the corrected graph was then found between the zero ordinate and that at selected values of the abscissa n .

Thus the integral

$$\int_0^n (d\mu/dn) dn = \mu_n - \mu_w \quad \dots \dots \dots (9)$$

was found, and hence, knowing μ_w , we are able to express μ_n in terms of n . The results of this calculation is given in Table V.

TABLE V.

	K Cl.	Na Cl.	K NO ₃ .
n	μ_n	μ_n	μ_n
0	1.3346	1.3346	1.3348
0.025	1.3379	1.3389	1.3372
0.05	1.3410	1.3430	1.3394
0.10	1.3471	1.3509	1.3437
0.15	1.3529	1.3585	1.3478
0.20	1.3585	1.3658	1.3519
0.25	1.3641	1.3729	...
0.2600	1.3568
0.2995	1.3694
0.3181	...	1.3823	...

Now Table IV. exhibits the values of μ_n , the refractive index of the solution at various points in the tube, deduced from Equation 7, in terms of l ; and we have also deduced μ_n in terms of n from Equation 9, and have expressed the results in Table V. Thus, by interpolation of the values given in Table IV., between those

shown in Table V., we are able to determine the concentration at any selected point in the tube. Some results are given below.

TABLE VI.

	K Cl.	Na Cl.	K NO ₃ .
<i>l</i> cm.	<i>n</i> gms./c.c.	<i>n</i> gms./c.c.	<i>n</i> gms./c.c.
0	0.0060	0.0056	0.0038
0.1	0.0126	0.0120	0.0080
0.2	0.0187	0.0184	0.0121
0.5	0.0380	0.0378	0.0248
1.0	0.0701	0.0705	0.0471
1.5	0.1012	0.1026	0.0708
2.0	0.1319	0.1346	0.0952
2.5	0.1616	0.1660	0.1207
3.0	0.1906	0.1968	0.1470
3.5	0.2188	0.2276	0.1744
4.0	0.2462	0.2579	0.2025
4.5	0.2731	0.2882	0.2312
5.0	0.2995	0.3181	0.2600

§ 10. RESULTS FOR K_n .

$$K_n = [i/(1-\delta)A] [Ft/h] [d\mu/dn] [(d-n+nd)/(d-n)] \quad \text{From Eq. 2 and 5a.}$$

We are now in a position to find the value of K_n , the coefficient of diffusion at a concentration n , from a knowledge of the four quantities enclosed in the square brackets, viz. :—

- A. The rate of change in the weight of the cell contents. (See § 4.)
- B. The deviation of the ray in passing through the cell. (See §§ 5-7.)
- C. The value of $[d\mu/dn]$ obtained by the interferometer. (See § 8.)
- D. The distribution of concentration down the diffusion tube. (See § 9.)

The results of the calculations indicated above are summarised in Tables VII., VIII., IX. following :—

TABLE VII.
Na Cl.

<i>l</i> cm.	<i>n</i> gms./c.c.	Normality gm.-eq./lit.	$K_n \times 10^5$ C.G.S. Curve 1, Fig. 6.	$K_n \times 10^5$ C.G.S. Curve 2, Fig. 6.
0	0.0055	0.095	1.237	1.247
0.1	0.0120	0.20	1.219	1.232
0.2	0.0181	0.31	1.205	1.218
0.5	0.0376	0.65	1.203	1.216
1.0	0.0705	1.20	1.230	1.242
1.5	0.1027	1.75	1.268	1.277
2.0	0.1346	2.30	1.307	1.312
2.5	0.1660	2.84	1.344	1.352
3.0	0.1968	3.36	1.379	1.387
3.5	0.2276	3.89	1.416	1.418
4.0	0.2579	4.41	1.451	1.444
4.5	0.2883	4.93	1.484	1.466
5.0	0.3181	5.44	1.511	1.485

TABLE VIII.

KCl.

l cm.	n gms./c.c.	Normality gm.-eq./lit.	$K_n \times 10^5$ C.G.S. Curve 3, Fig. 6.	$K_n \times 10^5$ C.G.S. Curve 4, Fig. 6.
0	0.0060	0.080	1.526	1.539
0.1	0.0126	0.17	1.496	1.513
0.2	0.0187	0.25	1.488	1.504
0.5	0.0380	0.51	1.508	1.523
1.0	0.0701	0.94	1.564	1.575
1.5	0.101	1.36	1.633	1.636
2.0	0.132	1.77	1.701	1.696
2.5	0.162	2.17	1.770	1.761
3.0	0.190	2.56	1.848	1.831
3.5	0.219	2.94	1.930	1.908
4.0	0.246	3.30	2.004	1.982
4.5	0.273	3.67	2.076	2.059
5.0	0.300	4.02	2.131	2.127

TABLE IX.

KNO₃.

l cm.	n gms./c.c.	Normality gm.-eq./lit.	$K_n \times 10^5$ C.G.S. Curve 5, Fig. 6.	$K_n \times 10^5$ C.G.S. Curve 6, Fig. 6.
0	0.0038	0.04	1.464	1.451
0.1	0.0080	0.08	1.446	1.432
0.2	0.0121	0.12	1.425	1.411
0.5	0.0248	0.25	1.381	1.367
1.0	0.0471	0.47	1.327	1.308
1.5	0.0708	0.70	1.289	1.266
2.0	0.0952	0.94	1.256	1.231
2.5	0.121	1.19	1.227	1.200
3.0	0.147	1.45	1.205	1.178
3.5	0.174	1.73	1.184	1.155
4.0	0.202	2.00	1.168	1.140
4.5	0.231	2.29	1.161	1.147
5.0	0.260	2.58	1.181	1.174

The results tabulated above are marked in accordance with the experimental curve in Fig. 6, from which they were respectively deduced, and are plotted graphically in Fig. 8, where they are represented by crosses + or ×, corresponding to the curves similarly marked in Fig. 6.

The points shown in triangles Δ are those obtained from the results of the author's previous researches, mentioned in the footnote in §1. The other points indicated in Fig. 8 are explained in the next paragraph, §11. From the graphs

Fig. 8 the following table can be constructed, giving a summary of all the results :—

TABLE X.

Normality gm.-eq./lit.	K Cl. $K_n \times 10^5$ C.G.S.	Na Cl. $K_n \times 10^5$ C.G.S.	K NO ₃ . $K_n \times 10^5$ C.G.S.
0.05	1.55	1.26	1.45
0.1	1.52	1.24	1.43
0.2	1.50	1.22	1.39
0.4	1.50	1.20	1.34
0.6	1.53	1.21	1.30
0.8	1.55	1.22	1.27
1.0	1.58	1.23	1.24
1.5	1.65	1.26	1.19
2.0	1.74	1.29	1.15
2.5	1.83	1.33	1.17
3.0	1.93	1.36	...
3.5	2.03	1.39	...
4.0	2.13	1.43	...
4.5	...	1.46	...
5.0	...	1.49	...

§ 11. RESULTS FOR DILUTE SOLUTIONS.

It will be observed that the results obtained in the present research, indicated in Fig. 8, agree with those previously obtained by the author by his earlier methods, except in the case of feeble solutions of potassium and sodium chlorides.

The author has no doubt that the present results are more exact, for in the earlier gravitational method much less accuracy was to be expected in the case of weak solutions than in that of stronger ones. In the method described in the present Paper, the optical measurements involved are no less accurate in the dilute solution near the top of the diffusion tube than they are in the stronger solutions beneath. A great deal of interest is associated with the diffusion of dilute solutions and many experiments have been made to test the results obtained in the weak solutions represented by the initial portions of the curves, Fig. 8.

The first point to be determined was whether the initial values of the coefficient, higher than were to be expected from the former investigations, might be due to some end-effect. This was examined by repeating the experiments as before, except that the bottle *M* (Fig. 3) was filled with a dilute solution ($n=0.02$ gm./c.c.) of the salt under investigation, instead of pure water. Thus a steady flow of weak solution passes over the diffusion tube, and the initial portion of the curves (Fig. 8) is eliminated, as under these conditions, concentrations less than $n=0.02$ are not obtained at all. There will be evidence of the existence of some end-effect, perhaps due to mechanical washing away of the salt in solution near the top of the diffusion tube caused by the current of liquid, if the experimental curve (Fig. 8) is found to bend upwards and still give abnormally high values in its initial portion; but if the results now obtained lie normally on the curve previously found when using a current of pure water, right down to the lowest concentration $n=0.02$, the absence of any such end-effect will be indicated.

As a result of the experiment, the dotted curves in Fig. 6, and the points shown

in Fig. 8 by circles, \odot , were obtained. The numerical results are tabulated in Table XI. below :—

TABLE XI.—*Dilute Solution Flowing over the Diffusion Tube.*

Na Cl.		K Cl.	
Normality.	$K_n \times 10^6$ C.G.S.	Normality.	$K_n \times 10^6$ C.G.S.
0.47	1.211	0.35	1.501
0.57	1.213	0.44	1.510
0.67	1.216	0.53	1.522
0.98	1.236	0.76	1.547
1.50	1.269	1.16	1.600
2.01	1.307	1.54	1.659
2.52	1.344	1.93	1.728
3.02	1.377	2.30	1.795
3.50	1.413	2.66	1.862

There is no sign of a minimum in the diffusivity within the range of concentration given above. Thus it appears that any end-effect is negligible, and the high values

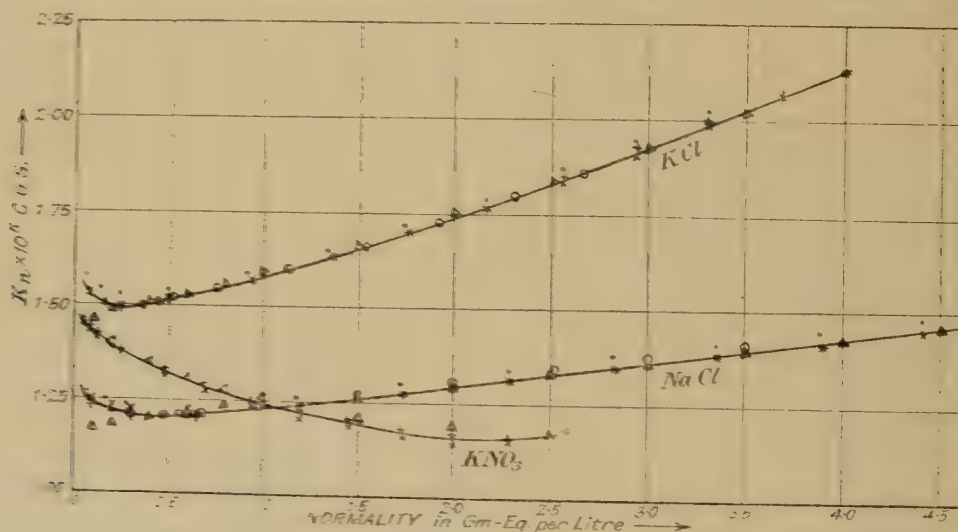


FIG. 8.

found for the diffusivity of the dilutest solutions in Table X. cannot be due to this cause.

The matter was then attacked by increasing the rate of flow of the water current through the diffusion cell. If there is any mechanical stirring up of the solution near the top of the tube, it must be increased if this current is augmented. An excessively rapid current will certainly have the effect mentioned, but it was found that considerably faster flows than those normally employed could be used without any considerable effect on the value of the coefficient of diffusion deduced from the observations. The experimental results indicated in Fig. 6 by the curves 7 and 8, and in Fig. 8 by dots (.) were obtained with water currents of about 85 c.c. per day.

A glance at the curves will show that flows of this order tend to reduce the value of h (see Fig. 6) and to make a small, but perceptible increase in the value of the diffusivity obtained. The actual numerical results are given in Table XII. :—

TABLE XII.—Water Current 85 c.c./day.

Na Cl.		K Cl.	
Normality.	$K_n \times 10^5$ C.G.S.	Normality.	$K_n \times 10^5$ C.G.S.
0.059	1.264	0.060	1.585
0.170	1.249	0.143	1.545
0.280	1.234	0.226	1.535
0.614	1.229	0.486	1.544
1.18	1.260	0.919	1.592
1.73	1.299	1.34	1.652
2.28	1.344	1.75	1.721
2.82	1.382	2.16	1.793
3.35	1.416	2.55	1.876
3.88	1.452	2.93	1.952
4.40	1.486	3.30	2.032

These figures show an increase in the value of the coefficient, compared with that given in Tables VII. and VIII. for similar concentrations, of about 1 or 2 per cent., but the substantial agreement between the results obtained with such water currents as were normally employed—50 c.c. per day—(indicated by the crosses in Fig. 8), and those found in the previous researches carried out by the author in which there was no flow at all (represented by the triangles in Fig. 8) appears to justify the assumption that the normal rate of flow is sufficiently slow to avoid those disturbances in the solution which may accompany more rapid currents of water.

In the case of KNO_3 we have a curve resulting from the investigation quite different from the other two shown in Fig. 8, but it is interesting to observe, as was pointed out to the author in 1916 by Prof. S. W. J. Smith, that curves like those shown for KCl and KNO_3 are to be expected on theoretical grounds. For moderate concentrations the experiments show that in KCl the diffusivity decreases with increase in dilution, i.e., according to Nernst's theory, $w/(u+v)$ decreases with increase in dilution, where u and v are the specific ionic velocities. In KNO_3 however, the experiments suggest an increase in $w/(u+v)$ as the dilution increases. This difference in the behaviour of the two salts must be due to their different anions, for they both possess the same cation. Now Hittorf has found that for solutions of moderate concentration, the transport number $v/(u+v)$ decreases with increase in dilution in KCl , and in the case of KNO_3 increases as the dilution increases, thus confirming in this respect the relative slopes of the experimental curves for these two salts.

In the cases of KCl and $NaCl$ it can be confidently stated that the experiments demonstrate that a minimum value exists in the diffusivity, and the position of this minimum value is estimated with fair accuracy at about 0.3 and 0.4 normal for the two salts respectively. In solutions diluter than that mentioned, the diffusivity increases on account of the rapid increase in ionisation of the salts in solution as the concentration approaches zero, and tends towards the limit theoretically deduced by Nernst for solutions of infinite dilution, viz., 1.70×10^{-5} ; 1.37×10^{-5} and

1.64×10^{-5} C.G.S. for K Cl, Na Cl, and K NO₃ respectively at the temperature employed in this investigation.

§ 12. CONCLUSION.

It will be recalled that Arrhenius, by his conception of the principle of ionic dissociation, enabled Nernst (*Zeitschr. f. ph. Chem.*, Vol. 2, p. 613, 1888) to apply this theory to the diffusion of dilute solutions of electrolytes, with the result that he deduced the well-known expression by means of which the coefficient of diffusion of such solutions was given in terms of the specific ionic velocities. In 1892 Arrhenius (*Zeitschr. f. ph. Chem.*, Vol. 10, p. 51, 1892) himself attempted to apply these methods to more concentrated solutions, and concluded that the coefficient of diffusion for electrolytes, with increasing concentration, should first fall from its value at infinite dilution on account of decreasing dissociation; and later, in more concentrated solutions, should increase on account of intermolecular attraction. Thus the coefficient for electrolytes should pass through a minimum value as the concentration is increased from zero. Arrhenius cites some results of Scheffer's experiments (*Zeit. f. ph. Chem.*, Vol. 2, p. 390, 1880), which suggest this minimum. Öholm (*Zeit. f. ph. Chem.*, Vol. 50, p. 309, 1904-5) also considered that he had observed some indication of the minimum expected by Arrhenius, but in his researches the "minimum" would appear to be associated with a quite considerable concentration, which not only is not in agreement with the deductions from Scheffer's experiments, but also is in itself improbable from our knowledge of the degree of dissociation connected with solutions of different concentrations.

In the experiments described in the present Paper, however, we have distinct reasons for believing that something similar to that predicted by Arrhenius has been actually observed, probably for the first time, and the graphs shown in Fig. 8 are remarkably similar to that given by Arrhenius (*Zeit. f. ph. Chem.*, Vol. 10, p. 88, 1892), as what was to be expected as a consequence of his theoretical speculations. Experimental confirmation of these speculations has not been achieved previously with any certainty on account of the great difficulty of obtaining sufficient accuracy when dealing with such dilute solutions. Extreme care must be taken to avoid even small disturbances of the solutions during experiment, and this necessity is not realised in many of the methods of investigation commonly adopted. For example, both Scheffer and Öholm employed a favourite method, in which the distribution of salt in the diffusing liquid is determined by syphoning the solution into a number of separate flasks and subjecting their contents to chemical analysis. It is obvious that it would be impossible to avoid disturbances in the liquid, inseparable from this method of experiment, which would be of quite a serious magnitude when dilute solutions are under investigation.

The experimental verification of Arrhenius' theory obtained in the research described in the present Paper has been achieved because the method not only employs the steady state of diffusion, in which the concentration at each point of the solution remains constant, while all the observations and measurements are made, and which greatly increases the probability of accuracy in the results; but also because, in this optical method, all sources of serious disturbance in the solution have been eliminated, and moreover, the measurements involved are liable to no more error in the case of dilute solutions than in those of much greater concentration. This fact is so contrary to what obtains in most processes of experiment that it makes

the method of particular value in the study of the diffusion of very dilute solutions. The chief point in doubt is the exact value of the concentration of the solution at the top of the diffusion tube. This is of no considerable importance until very dilute solutions are under consideration. For such solutions the value of the coefficient of diffusion can be determined, from the experimental observations described in this Paper, with greater accuracy than the exact value of the associated concentration. The general shape of the curves (Fig. 8) will be unaltered, but there may be a slight shift in the origin.

It may be claimed that the experiments described in this Paper not only demonstrate the existence of a minimum value in the diffusivity of certain salts dissolved in water, as was deduced from theoretical considerations by Arrhenius, and indicate the position of this minimum with considerable accuracy, but also for concentrations greater than about 0.25 normal, confirm the results previously obtained by the author by independent methods (*see* Footnote § 1), and it may be stated that the value of the coefficient of diffusion of such solutions is known with fair accuracy. We have discovered, moreover, the range of concentration which requires additional examination, and the author hopes to investigate these dilute solutions further in the near future.

The research has been carried out during the years 1920 to 1924 in the Physics Laboratories of Birkbeck College, and the author would like to express his gratitude to Prof. A. Griffiths, who not only suggested the investigation, but who has been always willing to assist with valuable advice and useful suggestions.

DISCUSSION.

The PRESIDENT expressed regret that the lateness of the hour precluded a discussion of the Paper. He considered that the scientific world is very much indebted to investigators at Birkbeck College, particularly Prof. A. Griffiths and Dr. B. W. Clack, for their experiments on diffusion. This admirable work had required the greatest patience, and it was extremely exact.

Prof. A. GRIFFITHS (communicated): In my opinion the work of Dr. Clack constitutes a very distinct advance in the study of diffusion through liquids. The agreement of the values of the coefficient of diffusion in the present work with those given by an earlier method, at all but feeble concentrations, is eminently satisfactory. The values of the results given by the present method at feeble concentrations are very cheering, leading one to hope that before long it will be possible to obtain numerical agreement between experimental results and theoretical conclusions. The present work of Dr. Clack indicates in the cases of the salts studied the range over which experimental results of still greater accuracy are required. I believe Dr. Clack has a choice of two or three methods of improving his work, and hope that he will have the honour of a final conquest of a most difficult branch of experimental study.

This is a maximum when $d/d_0 = \sqrt[6]{2} = 1.123$, which agrees moderately well with experience, as most materials rupture when the extension is of the order of 10 per cent.

For this value of d , the maximum stress $= 0.25 \times$ "molecular pressure," and the maximum inter-doublet bond $= 0.3257 \times$ equilibrium doublet linkage.

The stress-strain ratio or linear modulus of elasticity is

$$\varepsilon = \frac{df}{dd} = -6\kappa_2 d^{-7} + 12\kappa_2 d_0^6 d^{-13} \quad \dots \quad (3)$$

When $d = d_0$, this is

$$\varepsilon_0 = 6\kappa_2 d_0^{-7}$$

If the *volume* is reduced by 20 per cent. so that

$$d = \sqrt[3]{0.8} d_0 = 0.9283 d_0$$

then

$$\varepsilon = 21.45 \kappa_2 d_0^{-7} = 3.57 \varepsilon_0$$

implying that the linear modulus would be increased 3.57 times by a pressure which reduces the volume by 20 per cent.

Most actual materials *diminish* in linear elasticity under compression, but this is due to lateral yielding, and the only case which is suitable for comparison is that of bulk or volume elasticity.

The observed variations in the bulk modulus of *solids* under maximum experimental pressures (say 10,000 kilo/cm.²) are too small to be useful, and the values of the "molecular pressure" must be very high. Bridgman's results with *fluids* do, however, provide a comparison. He found that the bulk modulus of water increases to about $5\frac{1}{2}$ times its initial value under 12,000 atmospheres, the volume diminishing by 20 per cent. Presumably solids behave similarly under much greater pressures.

Writing the compression stress positive and using volumes ($v \propto d^3$)

$$p = av^{-4} - bv^{-2} \quad \dots \quad (4)$$

By equilibrium conditions when $p = 0$

$$a = bv_0^2$$

and

$$p = b(v_0^2 v^{-4} - v^{-2}) \quad \dots \quad (5)$$

$$\frac{\partial p}{\partial v} = b(-4v_0^2 v^{-5} + 2v^{-3})$$

and the compressibility

$$\beta = \frac{1}{p} \cdot \frac{\partial p}{\partial p} = \frac{1}{2b(v^{-2} - 2v_0^2 v^{-4})} \quad \dots \quad (6)$$

The product of the stress into the compressibility

$$p\beta = \frac{v_0^2 v^{-4} - v^{-2}}{2(v^{-2} - 2v_0^2 v^{-4})} \quad \dots \quad \text{from (5) \& (6)}$$

This is negative if $v < v_0$ and zero when $v = v_0$. If $v = cv_0$

$$p\beta = \frac{c^{-4} - c^{-2}}{2(c^{-2} - 2c^{-4})} \dots \dots \dots (7)$$

Bridgman's values in case of water from the Smithsonian Physical Tables and the calculated ones are given below :—

p (atmosph.)	$\beta \times 10^6$	c	$p\beta$	$(p+2500)\beta$	$\frac{c^{-4} - c^{-2}}{2(c^{-2} - 2c^{-4})}$
0	49	1.0	0	0.1225	0
200	43	0.991	0.0086	0.1161	0.0086
400	41	0.982	0.0164	0.1189	0.0171
500	39	0.978	0.0195	0.1170	0.0206
1,000	33	0.96	0.0330	0.1155	0.0369
12,000	9	0.80	0.1080	0.1305	0.1320
164,000	2.28*	0.50	0.214
984,000	0.239*	0.33	0.235
8,200,000	0.03*	0.20	0.245
*Hypothetical			calculated.		

The column headed $(p+2500)\beta$ is inserted to show that an assumed molecular pressure of 2,500 atmospheres gives a fairly constant product when added to the pressure and multiplied by the compressibility.

The conclusions to be drawn are thus :—

- (1) That the Born-Landé expression agrees with a linear expansion before rupture in solids of about 12 per cent. in any direction which conforms moderately well to the results of uni-directional tension experiments with non-plastic materials.
- (2) The space-rate of change of compressibility deduced from the same expression agrees very fairly well with the experimental results obtained with fluids under high pressures.

DISCUSSION.

Prof. A. O. RANKINE said that while he recognised that the numerical results of the theory were fairly consistent with experimental values, he could not help suspecting that this was a coincidence. What little is known of the nature of cohesion seems to indicate that the laws concerned must be far more complicated than a simple inverse power law. The doublets would only attract according to an inverse fourth-power law at a distance great compared with the distance apart of their components, not at the distances which actually obtain in a crystal; and, again, in a crystal the electron swarms of neighbouring atoms must be very close to one another in certain regions, and it is difficult to see why the particular law adopted in the Paper should hold. Further, the field of force round an atom must be regarded as having an axis, not as being spherically uniform and independent of direction. It seems unsatisfactory also to test a theory based on the structure of a solid crystal by measurements made on water in the liquid state.

Dr. D. OWENS said that, while he agreed with the previous speaker that the formulæ proposed in the Paper were open to objection, any hypothesis seemed better than none. Calculations such as the Author had made might be of value in suggesting limiting values of elasticity and density under great stresses; they permitted, for example, of interesting speculations as to the conditions of matter deep in the earth's interior.

AUTHOR'S reply (communicated): The author agrees with Prof. Rankine that the law must be far more complicated than a simple inverse power law, but thinks that a statistical average

effect might apply with different coefficients for different materials. The invalidity of the inverse fourth conditions at distances small compared with the separation of the doublet-components is mathematically certain, but the separation of the effective components may frequently be small, and in the case of alternate positive and negative ions the minimum ratio is not less than unity. The fields are certainly polarised, but the crystal packing suggests that in many cases there are three axes of maximum force and that the ellipsoid of attractive force would not differ greatly from a sphere. As to the use of water instead of solids for comparison of the rate of change of compressibility, it does not appear that the rates for solids have yet been measured with sufficient accuracy to be determinative, but they certainly tend to change in the same way.

He expresses his gratitude to Dr. Owen for reading the Paper. As to effects within the earth, by this analysis he has convinced himself for the first time that the high mean density of the earth must be due to high molecular weights and not to compression. On the general question of the validity of the approximation it is noteworthy that the changes with temperature produced anomalies. Near the melting point the law of repulsion must have almost the same form as the law of attraction.

DEMONSTRATION OF SUB-HARMONICS PRODUCED BY A TUNING-FORK.

By W. N. BOND, *M.Sc.*, University College, Reading.

THE experiments demonstrated were an extension of those described in a letter to *Nature* of March 8, 1924, and comprised the production of notes of frequencies equal to submultiples of that of the tuning-fork, their emission depending on the production of forced intermission at the contact of the fork stem and a sounding-board or metal block.

The note an octave below that of the fork, which has been observed by other workers, was produced. Then notes of one-third and one-quarter of the frequency of the fork were sounded. Experiments by R. G. Durrant described in *Nature* a number of years ago, in which a water jet controlled by a tuning-fork produced a note an octave below that of the fork, were mentioned as being the most similar experiments known to the author. A sonometer experiment to test the frequencies of the notes was described. The notes were shown to be due to intermittent contact of the fork and metal block by completing a circuit containing an ammeter and loud-speaking telephone. The ammeter showed different mean currents for different sub-harmonics.

Graphical records were shown which had been obtained by inserting a Deprez telegraphic signal marker in the circuit, the results being summarised in the following table:—

Fundamental	288.8 ± 1.0	...	(288)
1st sub-harmonic	144.4 ± 0.3	...	(144)
2nd	„	95.6 ± 0.2	...	(96)
3rd	„	71.5 ± 0.3	...	(72)
4th	„	58.4 ± 0.5	...	(57.6)

The possibility of the experiments having some bearing on the theory of audition was mentioned.

Mr. Bond thanked Dr. D. Owen for his interest in the experiments, Mr. A. W. P. Wolters for the loan of the apparatus, and Mr. R. C. Walker for help in the experiments.

Communicated subsequently: During the later experiments the author found that the possibility of the existence of sub-harmonics has been mentioned by J. L. Dunk in his books on Tonality, the term "coincidental series" being used to describe them.

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